Identification, molecular characterisation and significance of fire residues in colluvial soils from Campo Lameiro (NW Spain)

Identificación, caracterización molecular y significado de los residuos de fuego en los suelos coluviales de Campo Lameiro (NO Peninsular)

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Santiago de Compostela, 2010

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INFORMAN

Que la presente memoria, titulada "Identification, molecular characterisation and significance of fire residues in colluvial soils from Campo Lameiro (NW Spain)", realizada por el doctorando Joeri Kaal para optar al grado de Doctor, reúne todos los requisitos y condiciones necesarias como trabajo de Tesis doctoral.

Y para que conste, dan el visto bueno para su presentación ante la Comisión de Doctorado de la Universidad de Santiago de Compostela.

En Santiago de Compostela, a 16 de noviembre de 2010.

Fdo. D. Antonio M. Martínez Cortizas D. Felipe Criado Boado

Contribuciones en congresos y artículos basados en los trabajos de investigación que culminaron en la elaboración de la tesis:

Artículos:

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Kaal, J., van Mourik, J.M, 2008. Micromorphological evidence of black carbon in colluvial soils from NW Spain. *European Journal of Soil Science* 59, 1133-1140.

Kaal, J., Costa Casais, M., Ferro Vázquez, C., Pontevedra Pombal, X., Martínez Cortizas, A., 2008. Soil formation of "Atlantic rankers" from NW Spain - A high resolution aluminium and iron fractionation study. *Pedosphere* 18, 441-453.

Kaal, J., Martínez Cortizas, A., Buurman, P., Criado Boado, F., 2008. 8000 years of black carbon accumulation in a colluvial soil from NW Spain. *Quaternary Research* 69, 56-61.

Kaal, J., Martínez Cortizas, A., Nierop, K.G.J., Buurman, P., 2008. A detailed pyrolysis-GC/MS analysis of a black carbon-rich acidic colluvial soil (Atlantic ranker) from NW Spain. *Applied Geochemistry* 23, 2395-2405.

Kaal, J., Martínez Cortizas, A., Eckmeier, E., Costa Casais, M., Santos Estévez, M., Criado Boado, F., 2008. Holocene fire history of black colluvial soils revealed by pyrolysis-GC/MS: a case study from Campo Lameiro (NW Spain). *Journal of Archaeological Science* 35, 2133-2143.

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Kaal, J., Rumpel, C., 2009. Can pyrolysis-GC/MS be used to estimate the degree of thermal alteration of black carbon? *Organic Geochemistry* 40, 1179-1187.

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Carrión, Y., Kaal, J., López-Sáez, J.A., López-Merino, L., Martínez Cortizas, A., 2010. Holocene vegetation change in NW Spain revealed by anthracological and palynological records from a colluvial soil. *The Holocene* 20, 53-66.

Kaal, J., Carrión, Y., Asouti, E., Martín Seijo, M., Costa Casais, M., Martínez Cortizas, A., Criado Boado, F., *in press*. Long-term deforestation in NW Spain: Linking the Holocene fire history to vegetation change and human activities. *Quaternary Science Reviews,* doi: 10.1016/j.quascirev.2010.10.006.

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Kaal, J., Martínez Cortizas, A., Criado Boado, F. 8000 years of fire-induced molecular modifications in Campo Lameiro (NW Spain) (póster). European Geosciences Union, General Assembly, abril 2007, Viena, Austria.

Kaal, J., Martínez Cortizas, A. Pyrolysis-GC/MS of Black Carbon: fresh knowledge of the molecular structure of aged charcoal (presentación oral). 18th International Symposium on Analytical and Applied Pyrolysis, mayo 2008, Costa Teguise, España.

Kaal, J. Pyrolysis-GC/MS of Black Carbon: past and future (póster). European Geosciences Union, General Assembly, abril 2009, Viena, Austria.

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TABLE OF CONTENTS

ABBREVIATIONS

BC = Black Carbon
B*n*CA = benzene with *n* carboxylic acid groups
BPCA = benzene polycarboxylic acid
CIDAR = Rock Art Interpretation and Documentation Centre
CP = cross polarisation
DP = direct polarisation
ESR = electron spin resonance
FT-ICR = Fourier transform ion cyclotron resonance
GC = gas chromatography
Gt = gigatonne (10^{15} g)
IR = infrared
MMM = molecular mixing model
MS = mass spectrometry
NEXAFS = near-edge X-ray absorption fine structure
NMR = nuclear magnetic resonance
OAVS = ocean, atmosphere, vegetation, soil
PAH = polycylic aromatic hydrocarbon
SEM = scanning electron microscopy
SOM = soil organic matter
THM = thermal hydrolysis and methylation
TMAH = tetramethylammonium hydroxide
TQPA = total quantified peak area

SUMMARY

The Rock Art Interpretation and Documentation Centre (CIDAR)[1] in Campo Lameiro (Pontevedra, Galicia, NW Spain) is destined to be inaugurated in 2010. This visitor and research center is surrounded by numerous rock art panels (petroglyphs), i.e. the so-called Rock Art Park of Campo Lameiro. The petroglyphs were created between approximately 4500 and 2500 calibrated years before present (cal BP). Due to the scarcity of cultural remains obtained from excavations, little is known of the activities of the societies that created and used the rock art, casting doubt on the chronology and function of the petroglyphs.

The soils in the Rock Art Park are black-coloured colluvial deposits, some of which are very thick (> 1 m). These soils, referred to as Atlantic rankers, formed upon Holocene slope transport processes (erosion/sedimentation) since ca. 12,000 cal BP. The depth sequence of these soils can be considered as physical archives of past environments. Hence, in 2003 soil columns were collected from mechanical trenches in order to generate palaeo-environmental information (slope stability, rock exposure, climatic conditions, acidification, etc.), focussing on the geochemical signals from inorganic phases. Initially, studies of the organic material were restricted to elemental analysis and selective extraction studies. In 2005 an attempt was undertaken to acquire archaeological and palaeo-environmental information from the soil organic matter (SOM) by advanced molecular approaches that had hitherto not been applied to the enigmatic SOM in this soil type –an attempt of which the results are presented in this thesis.

Preliminary analyses of the SOM demonstrated that the soils in the Rock Art Park contained large amounts of fire residues (Black C, BC) in virtually all layers, suggesting an important role of fire in the history of the study area. The identification, molecular characterisation and significance (palaeo-environmental and archaeological) of these fire residues form the subject of this thesis, the contents of which will be summarised in the next paragraphs.

[1] A project of the Council for Culture, Social Communication and Tourism. It forms part of the *Galician Network for Archaeological Heritage* (RGPA), together with the Roman constructions in Lugo, the Castro culture park in San Cibrán de Lás (Ourense) and the megalithic park of the Costa da Morte (A Coruña).

I. Black Carbon stored in colluvial soils from NW Spain

A significant proportion of the organic matter stored in soil PRD-1 from the Rock Art Park of Campo Lameiro has a pyrogenic origin (**Manuscript 1**). This was concluded from the exceptionally large proportion of pyrolysis products that are commonly assigned to BC, notably benzenes and polycyclic aromatic hydrocarbons (PAHs). The abundance of BC was confirmed by the dominant resonances from aromatic ^{13}C atoms in solid-state ^{13}C nuclear magnetic resonance (NMR) analysis of selected samples. The proportion of the 'molecular indicators of BC' (this is a tentative statement supported by the methodological pyrolysis studies presented in Manuscripts 4–6) was independent of macroscopic (> 2 mm) charcoal content. Aqueous sodium hydroxide-extractable BC was much more abundant than BC in macroscopic charcoal. These results suggested that fires had occurred on a regular basis for the last 8000 years. Chemical markers of past vegetation, animal residues and possibly artefacts of human activities (except for fires perhaps) were not detected in the SOM, which may be attributed to a combination of pre-depositional thermal degradation (fire) and, more importantly, post-depositional degradation during storage in the soil (abiotically and biologically).

Manuscript 2 focuses on the chemical characteristics of the SOM in soil PRD-1, as revealed by pyrolysis gas chromatography/mass spectrometry (pyrolysis-GC/MS) of the NaOH-extractable SOM and a selection of macroscopic charcoal fragments. The pyrolysis fingerprint of the aged charcoal was used to aid in the recognition of BC in the extractable fraction, because detailed descriptions of pyrolysis-GC/MS data on BC, and especially aged BC, were not available. The pyrolysates from the macroscopic charcoal were dominated by benzene, benzonitrile and PAHs (60–98 % of total quantified peak area; TQPA). These pyrolysis products accounted for 21–54 % of TQPA in the extractable fraction thus confirming the abundance of BC in the fine fraction of the soil. Apart from BC, the pyrolysis products of degraded SOM (from lignin, protein and carbohydrates) and lipids (either degraded or intact) were abundant. It was concluded that the prevalence of BC might be partly responsible for the long-term stability, or recalcitrance, of the SOM. The abundance of reactive Al (oxy)(hydr)oxides further protects the BC and non-charred organic matter against biological decay through sorptive preservation. Only small proportions of the pyrolysis markers of intact biomass, such as levoglucosan from cellulose and methoxyphenols from lignin, were detected, and these proportions rapidly diminished with depth, suggesting a high degree of degradation (or 'humification') of the SOM. Thus, the formation of organo-mineral complexes preserves degraded SOM and not the relatively intact biomass (recognisable biopolymers). These results present new insights into the pedogenesis of Atlantic rankers, which was thus hypothesised to be intimately associated with the palaeofire regime. Furthermore, there was no

indication for podzolisation in the pyrolysis signature from PRD-1, which supports previous work from the study area (Kaal et al., 2008) in that the vast majority of the organic constituents of the soil is immobile or hardly mobile. This study presents the first detailed fire record obtained by molecular characterisation of SOM.

The fire history as revealed by pyrolysis-GC/MS of soils PRD-1 and PRD-2 was then interpreted from a chronological perspective (**Manuscript 3**). Applying statistical analyses to the composition of the pyrolysates, eight different phases with different SOM composition –reflecting changes in fire frequency and intensity– were identified. It appeared that the first fires occurred before 8500 cal yrs BP. The increased proportion of benzenes and PAHs suggested an intensification of the fire regime in the Mesolithic/Epipalaeolithic-Early Neolithic (8500–6000 cal BP), which corresponds to the wet and warm Holocene Thermal Maximum period. Around 6000 cal BP a shift in the relative proportions of benzenes and PAHs points towards a change in fire conditions and/or fuel source (as appeared later on, from tree- to shrub-dominated). From ca. 6000 cal BP until ca. 2000 cal BP the rapid sedimentation of homogeneous BC-rich material suggested the frequent burning and associated erosion/sedimentation during the Neolithic, the Bronze Age and the Iron Age. This period encompasses the cold period of Neoglaciation during which natural fires (e.g. by lightning or rockfall) would have been less frequent, suggesting that the fires were anthropogenic. Then, probably in the Late Roman/Germanic period, a layer with an even higher proportion of BC was deposited, followed by a gradual decline towards the surface of the soils, where intact biomass is more abundant.

These results suggested a strong effect of fire on SOM chemistry and the changes detected are in agreement with the human-driven fire regime of other mid-altitude regions in Western and Central Europe: fire-induced accelerated erosion and deforestation around 6000 cal BP, which corresponds to the Neolithic shift towards an agricultural society, followed by a long-term regime of frequent fires (even though the number of fires cannot be established reliably from colluvial deposits). The shrub-dominated open landscape of NW Spain would thus be intimately associated with prehistoric burning, at least in part inflicted by past societies.

II. Methodological studies on identification and molecular characterisation of aged Black C

Manuscripts 4, 5 and 6 transmit methodological work that aimed to recognise, characterise and quantify aged BC. These studies were considered necessary as the interpretations in Manuscripts 1–3 remained somewhat tentative because of the issues involved in identifying aged BC from complex SOM admixtures, especially in the opinion of workers without experience in pyrolysis-GC/MS.

Selected samples of NaOH-extractable organic matter and macroscopic charcoal were analysed by a series of advanced molecular characterisation methods that are commonly applied in BC research, in addition to analytical pyrolysis techniques (**Manuscript 4**): pyrolysis-GC/MS, Thermally assisted Hydrolysis and Methylation GC/MS (THM-GC/MS), two types of solid-state ^{13}C NMR (cross and direct polarisation; CP and DP NMR) and the benzene polycarboxylic acid (BPCA) method. The NaOH-extractable organic matter consisted of 30–50 % BC according to DP NMR, which is considered the most quantitative technique of the methods applied. The BPCA method provided lower estimations probably because it assesses large polyaromatic clusters of BC while, according to current theories on how the method operates at the molecular scale (following Ziolkowski and Druffel, 2009), any BC moiety of less than three fused aromatic rings is likely to escape the method. The low degree of condensation of the BC studied is most likely caused by abiotic and/or biological decay processes occurring in the soil, principally oxidation (carboxylation) and depolymerisation. Indeed, benzenepolycarboxylic acids were detected in the thermochemolysates of the extracted SOM (from THM-GC/MS), showing that carboxylic groups were abundant naturally and therefore that part of the microscopic/amorphous BC is indeed strongly oxidised. Finally, the BC in the extractable fraction appeared as SEM amorphous highly carboxylated fine-grained moieties, in addition to microscopic and macroscopic fragments that could be easily recognised visually. Combined results suggested that at least 30–40 % of the extractable SOM originates from fire residues, which situates the soils of Campo Lameiro among the world's richest in BC (analysed so far).

Manuscript 5 presents an attempt to quantify the amorphous fine-grained BC by means of thin sections analysis. It also aimed at providing additional evidence for the hypothesis that a significant fraction of the SOM originated from fire residues. Unfortunately, automatic image analysis did not allow us to quantify the darkest portion of the organic matter, which was at least partly derived from fire residues. Some opaque mineral fragments gave equally dark pixels and part of the BC, especially that near pores in large fragments, gave a relatively light pixel value (in the range of dark-coloured yet probably non-fire derived SOM) because of reflectance issues that could not be evoked by lowering the light intensity –in that way the light-coloured and dark/black-coloured SOM would become indistinguishable in colour histograms. Nonetheless, the micromorphological study was meaningful because it allowed to (1) reinforce the abundance of BC in many sizes and shapes in the soils, (2) identify biological decay of BC by the presence of xylophague casts in charcoal fragments (at the time this study was performed many authors still considered BC virtually 'inert') and (3) identify BC incorporation into the fine fabric of the soil, as recognised by the welded modexi (excremental fabric) inside charcoal fragments that resembled the microgranular matrix of the SOM in

III. Holocene fire history of Campo Lameiro

Analytical pyrolysis has limited capacities to elucidate the botanical source of burning residues, which is a consequence of the thermal modifications that tend to efface the differences in molecular composition between plants. Therefore, other tools were needed to elucidate the fire history of the area and its relation to vegetation change and human activities.

The botanical source of pollen (palynology) and charcoal (anthracology) from soil PRD-2 was determined to investigate the link between vegetation change and the fire regime of the last ca. 6300 yrs (**Manuscript 7**). It was found that until ca. 6000–5500 cal BP the site was covered with deciduous oak (*Quercus* cf. *Q. robur*) forming an open habitat with conspicuous grasses, ferns and shrubs in the understory. Then, shrub communities that do well in fire-prone areas expanded relative to oak, probably as a result of fire. Additional phases of degradation of the oak forest occurred ca. 4000–3500 cal BP and ca. 2500 cal BP, which coincided by increases of woody Fabaceae and/or *Erica* cf. *E. arborea.* Heather was dominant from ca. 1700 cal BP onwards in both pollen and charcoal records, when the presence of a thick charcoal-rich layer in the soil confirms the link between forest retreat and fire. Younger material showed the formation of a mature heathland (evidenced by a decline in the degree of growth ring curvature).

Generally, these changes were more pronounced in the charcoal than in the pollen record. This is not surprising as pollen is easily transported through the action of wind and thus provides information on a regional scale while charcoal, especially the macroscopic fragments (> 2 mm) used for this study, is not transported over significant distances and therefore has a more local origin. Another important discrepancy between charcoal and pollen records was the profusion of charcoal from Fabaceae (broom and gorse) yet few pollen were detected from these species, probably because of their rapid and almost complete pollen deterioration in Atlantic rankers (following van Mourik, 1986). Fire-induced deforestation was concentrated on the upper part of the hill (the study area), allowing for significant inflow of tree pollen (*Betula* sp., *Quercus* sp., and *Alnus* sp.) from the surrounding valley and lower-slope vegetation. Deforested upper slopes and flats (*o monte*) covered by black-coloured colluvium are ubiquitous in NW Spain. They are often surrounded by lower-slopes and valleys that harbour arboreal vegetation. The omnipresence of synanthropic pollen indicators (*Plantago lanceolata, Urtica dioica*) that are typical of an area subjected to local animal grazing suggested that the area was used as pasture since at least ca. 6000–5500 cal BP onwards. It was thus postulated that the vegetation was deliberately ignited by past societies to produce pasture.

most of the horizons studied. For the first time it was shown that biological attack allowed for the conversion of morphologically recognisable BC to amorphous particles entangled with the mineral and non-BC fractions of the soils. This may explain the discrepancy between the macroscopic charcoal content and the chemical fingerprint of the SOM (see Manuscript 2). Finally, the abundance of fungal sclerotia –see Manuscript 4/Figure 1b, and Manuscript 5/Figure 4a– probably from *Cenococcum geophilum* (a species that is frequently encountered in materials that are enriched in BC; Alonso and López, 2005) might suggest that fungi played a significant role in BC decomposition.

Using new instrumentation, artificial charring during pyrolysis in pyrolysis-GC/MS was studied in order to determine optimal conditions for the study of BC using pyrolysis-GC/MS (**Manuscript 6**). This pyrolysis device is a Pt filament resistive heating pyrolyser (Pyroprobe 5000, CDS) and not a Curie-Point pyrolyser that was used for earlier work and most other pyrolysis studies that can be found in literature. The resistive heating pyrolyser allows for varying the pyrolysis temperature. To compare the pyrolytic behaviour of BC and non-pyrogenic organic matter sample, an aged charcoal sample from Campo Lameiro and a peat sample from *Pena da Cadela* bog (NW Spain) were used. These samples were pyrolysed at 400–1200 ºC in order to monitor artificial charring to the peat sample (in the pyrolysis chamber) and witness changes in pyrolysis signature for the charcoal. It was concluded that the optimum pyrolysis temperature was 750 ºC. At this pyrolysis temperature, artificial charring is limited yet the BC is pyrolysed to such an extent that good spectra are obtained. This pyrolysis method was then applied to 91 charcoal fragments from soil PRD-4 from Campo Lameiro, which contains macroscopic charcoal ranging from recent to > 11,000 years old, in order to study differences in pyrolysis fingerprint with age and plant source (birch, oak and legumes, determined anthracologically).

The pyrolysate composition of these plant species was surprisingly similar for charcoal obtained from the same soil layer (equal age), while large differences were found with age: recent charcoal contains significant amounts of non- or weakly-charred chemical groups while the aged charcoal is dominated by the markers of the more severely thermally modified fraction of the BC. It seems as if BC becomes more susceptible to pyrolysis upon ageing. This may be explained by depolymerisation reactions of the more strongly-condensed fraction, and might explain the relatively poor quality of spectra obtained from strongly charred recent BC specimen. Furthermore, the improved method allowed for the detection of a large array of N-containing pyrolysis products so far unknown to be produced from vegetation-derived BC, such as C_1-benzoxazole, benzene dicarbonitriles, 2-phenylpyridine, naphthalenecarbonitrile and 2-biphenylcarbonitrile, later to be confirmed by Song and Peng (2010).

An anthracological study of the five PRD soils from the Campo Lameiro area allowed us to further elaborate the fire history reconstruction of the area, improve the time resolution of the changes detected and extend the record to the last ca. 13,000 years (**Manuscript 8**). The vegetation of the Early Holocene (ca. 13,000–10,000 cal BP) was dominated by *Betula* sp. (birch), shrubs (Fabaceae) and probably abundant herbaceous understory. The area was then colonised by deciduous oak, forming a well-developed natural forest from ca. 10,000 cal BP until ca. 5500 cal BP. A decline in deciduous *Quercus* and increase in *Arbutus unedo* and Fabaceae ca. 7000–6500 cal BP might be indicative of early forest clearance by Late Mesolithic/Epipalaeolithic societies. Then, around 5500 cal BP, the vegetation changed radically because of fires, as mentioned earlier. This was a major episode of fire-induced destruction of deciduous forest. Other phases of accelerated environmental degradation (deforestation, erosion, acidification) occurred ca. 4000–3500 cal BP, 3000–2000 cal BP and 2000–1500 cal BP. These changes were reflected in the charcoal of the majority of the soils, although at site PRD-4, which has the lowest altitude, the disappearance of deciduous forest (represented by *Quercus* sp.) seemed to have occurred much later than at the other sites (after ca. 2000 cal BP). Oak recovered partially after these episodes, with the exception of the last phase in the Late Roman/Germanic period which caused the definitive settlement of *Erica*-dominated shrub communities.

The various expansion phases of shrub communities (*Erica* sp. in particular) coincided with known periods of augmented deforestation and human impact in NW Spain, such as the large-scale deforestation of Western and Central Europe in the Neolithic (6000–5500 cal BP event), the impact of mining activities and population increase during the Late Bronze Age and the Iron Age (3000–2000 cal BP event) and the Roman/early Germanic periods (2000–1500 cal BP event). Interestingly, some of these phases coincide with periods of rapid climate change, suggesting that a link may exist between environmental change and changes in human behaviour: changes in ecosystem response to human interference and/or changes in human activities as a response to environmental change. Considering the evidence of pollen analyses from soil PRD-2 (Manuscript 7), the phases of vegetation change were probably the result of frequent anthropogenic burning to generate pasture, effectively inhibiting regeneration of *Quercus*-dominated forest vegetation. The present-day vegetation patterns and fire culture of *o monte* should thus be viewed as the outcome of long-term human activities in the area, starting in the Neolithic or possibly already in the Mesolithic/Epipalaeolithic. These results are in general agreement with the evidence obtained by molecular characterisation of the SOM.

IV. Synthesis

The major findings of the present research can be summarised as follows: the Atlantic rankers in the Rock Art Park of Campo Lameiro contain large amounts of BC from palaeofires. The vast majority of this BC is strongly oxidised and depolymerised. It resides in soil micro-aggregates mixed with non-pyrogenic SOM and inorganic constituents, including poorly crystalline Fe and Al phases, which enhance the preservation of BC in the soils. The black colour and exceptional chemical recalcitrance of the SOM from Atlantic rankers may thus be at least partially attributed to the abundance of BC. The BC had accumulated in the soils during a continuous Holocene fire regime that inhibited local forest recovery. This fire regime is probably the main factor in the prehistoric deforestation of *o monte* in Galicia (NW Spain), which initiated ca. 7000–6500 cal BP and intensified during several phases after that (ca. 5700–5300 cal BP, 4000–3500 cal BP, 3000–2000 cal BP y 2000–1500 cal BP). Forest retreat was concentrated on the upper slopes of the Monte Paradela hill (i.e., the Rock Art Park area), while valleys and lower slopes remained largely intact. It seems that during the days of rock art creation (ca. 4500–2500 cal BP) the oak-dominated deciduous forest was already largely destroyed. Human activities played a major role in the fire regime and therefore the deforestation and concomitant expansion of fire-tolerant shrubland and erosion at *o monte* in NW Spain were initiated by prehistoric societies.

RESUMEN

El Centro de Interpretación y Documentación del Arte Rupestre (CIDAR)[2] en Campo Lameiro (Pontevedra, Galicia, NO Peninsular) está destinado a ser un lugar de visita para turistas y expertos en la materia, así como sede de exposición, divulgación y protección del patrimonio arqueológico, y a desempeñar labores de investigación científica y técnica. Este centro, que probablemente será inaugurado a finales del año 2010, está rodeado por grabados de arte rupestre (petroglifos), formando el nombrado Parque Arqueológico de Arte Rupestre de Campo Lameiro. Cabe apuntar que los petroglifos se crearon, aproximadamente, entre hace 4500 y 2500 años antes del presente (cal BP). Como consecuencia de la escasez de artefactos arqueológicos en las excavaciones, se desconocen las actividades de las sociedades creándose un escenario de incertidumbre sobre la cronología y la función de la cultura rupestre.

La cobertura edáfica del Parque Arqueológico de Arte Rupestre son mayoritariamente suelos coluviales de intenso color negro, algunos de gran potencia (> 1 m de espesor). A estos suelos se les denomina Ranker Atlántico y se forman a través de la erosión/sedimentación desde inicios del Holoceno. Por lo tanto, son archivos que contienen un registro físico de los cambios ambientales. En el año 2003 se tomaron columnas de suelo para su análisis y con el fin de generar conocimiento paleoambiental (estabilidad geomorfológica del suelo, exhumación de rocas, cambios en las condiciones climáticas, acidificación, etc.), dando gran relevancia a las señales geoquímicas de las fases inorgánicas. Apuntar, en este sentido, que inicialmente los estudios de la materia orgánica se limitaron, de modo más preciso, al análisis elemental y las extracciones selectivas. Fue en el año 2005 cuando se inició un estudio cuyo objetivo era proporcionar información arqueológica y paleoambiental aplicando una metodología avanzada para el estudio de la composición molecular de la materia orgánica del suelo (MOS). Este estudio es el objetivo de la presente tesis. Una circunstancia que hay que matizar es que hasta entonces no se había llevado a cabo ninguna caracterización molecular de la MOS típica del Ranker Atlántico.

Los análisis de la composición molecular de la MOS demostraron que los suelos del Parque Arqueológico de Arte Rupestre contienen cantidades considerables de residuos de fuego (*Black Carbon*, BC) en todos los niveles. Estos resultados apuntan a que el fuego jugó un papel importante en la historia de la zona estudiada. La identificación, la caracterización molecular y el significado de este BC forman el cuerpo de esta tesis, contenido que resumiremos y daremos cuenta a continuación.

[2] Proyecto adscrito a la Consellería de Cultura Comunicación Social y Turismo, y que conforma la *Rede Galega de Patrimonio Arqueolóxico* (RGPA), junto con el parque del mundo romano de Lugo, el parque de la cultura castreña en San Cibrán de Lás (Ourense), y el parque de megalitismo de la Costa da Morte (A Coruña).

I. *Black Carbon* en los suelos coluviales del NO Peninsular

Una proporción significativa de la MOS acumulada en el suelo PRD-1 del Parque Arqueológico de Arte Rupestr de Campo Lameiro es de origen pirogénica (**Manuscrito 1**). Esta conclusión se explica por la proporción excepcionalmente alta de productos de pirólisis que se atribuye, habitualmente, al BC, tales como los bencenos y los hidrocarburos aromáticos policíclicos (HAPs). Las resonancias dominantes de átomos ^{13}C en grupos aromáticos en los espectros de Resonancia Magnética Nuclear (RMN) en estado sólido confirmaron la abundancia del BC. La proporción de los 'indicadores moleculares de BC', afirmación tentativa que se ve sostenida por los estudios metodológicos de pirólisis presentados en los Manuscritos 4–6, es independiente del contenido en carbón macroscópico (> 2 mm). Consecuentemente, la abundancia de BC en extractos de sosa (NaOH (aq)) es mucho mayor que la del BC en carbón macroscópico. Estos resultados revelan que los incendios ocurrieron de forma habitual durante los últimos 8000 años. No se detectaron marcadores químicos de vegetación específica del pasado, ni residuos de fauna, ni artefactos de actividad humana (excepto, tal vez, el fuego), hecho al que se puede atribuir una combinación de degradación térmica pre-deposicional (fuego) y, probablemente más significativo, degradación biológica pos-deposicional.

El **Manuscrito 2** se orienta hacia las características químicas de la MOS en el suelo PRD-1, utilizando los datos de pirólisis-cromatografía de gases/espectrometría de masas (pirólisis-CG/EM) de fragmentos de carbón macroscópico y de la MOS extraíble en NaOH. Dada la escasa información disponible sobre la conducta pirolítica del BC, especialmente en el caso de BC antiguo, se analizó carbón vegetal del mismo suelo para poder utilizar, comparativamente, la huella pirolítica del carbón antiguo, y así reconocer productos del BC antiguo en los extractos de NaOH. Los bencenos, el benzonitrilo, y los HAPs representan un 60–98 % de los pirolisatos (porcentaje del área cuantificada total, ACT) del carbón macroscópico. Estos productos de pirólisis representan el 21–54 % del ACT de la fracción extraíble en NaOH, confirmando así la abundancia de BC en el extracto y, por lo tanto, en la fracción fina de suelo. Consecuentemente, la resistencia frente a la degradación, inherente al BC, puede explicar la estabilidad de la MOS a largo plazo. Aparte de BC son abundantes los productos de pirólisis de la MOS degradada no-pirogénica (derivada de ligninas, proteínas, lípidos y carbohidratos). No obstante, la alta concentración de óxidos, hidróxidos y oxihidróxidos de Fe y Al, de baja cristalinidad, protege al BC oxidado y a la MOS no-pirogénica frente a la descomposición biológica debido a su adsorción a estos componentes del suelo (enmascaramiento de grupos funcionales). La proporción de productos de pirólisis de MOS, intacta o poco degradada, como el levoglucosán, derivado de la celulosa y los compuestos metoxifenólicos de la lignina, es muy baja en la superficie del suelo (< 5 % del

ACT), e incluso está por debajo del límite de detección (ca. 0.2 %) en la parte inferior del suelo, lo que confirma el alto grado de degradación de la MOS. Con toda seguridad la MOS no-pirogénica, que se encuentra estabilizada en complejos órgano-minerales, está altamente degradada. El efecto protector del Al y, en menor medida, del Fe poco-cristalino no afecta a la MOS fresca (biopolímeros reconocibles). Cabe inferir, que estos resultados representan nueva información sobre la génesis de los Ránkeres Atlánticos: su formación está, rigurosamente, relacionada con el régimen de paleoincendios. No se encontró ninguna evidencia de podzolización en los datos de pirólisis-CG/EM de PRD-1, hecho que se reafirma con un trabajo geoquímico del mismo suelo en el cual se concluyó que la MOS no ha sufrido movilización (Kaal et al., 2008). Este estudio constituye el primer registro de paleoincendios basado en la caracterización molecular de la MOS.

La interpretación cronológica de la historia de los incendios y su relación con la actividad humana, tal como revela la pirólisis-CG/EM de los suelos PRD-1 y PRD-2, se describe en el **Manuscrito 3**. Aplicando análisis estadísticos, se identificaron ocho fases en la composición de la MOS, reflejando fases distintas en la frecuencia y en la intensidad de los incendios. Los primeros incendios detectados en estos suelos son anteriores al 8500 cal BP. Un incremento en la proporción de bencenos y HAPs sugiere una intensificación en el régimen de los incendios alrededor del 8500–6000 cal BP, lo que corresponde al Mesolítico/Epipaleolítico y el Neolítico temprano en la cronología arqueológica, y al período húmedo y cálido del Máximo Térmico del Holoceno (o 'Hipsitermal') en la cronología climatológica. Una variación en las proporciones relativas de bencenos y HAPs ca. 6000 cal BP indica un cambio en las condiciones de los incendios y/o la naturaleza del combustible, más tarde germinará la tesis de que fue el cambio de una vegetación, en particular de vegetación arbórea, a una otra dominada por arbustos (matorral). La relativamente rápida sedimentación de material homogéneo y rico en BC, desde aproximadamente 6000 cal BP hasta ca. 2000 cal BP, apunta a la existencia de un sistema recurrente de incendios y erosión durante el Neolítico, la Edad del Bronce y la Edad del Hierro. Este período incluye un episodio climático largo y frío, la 'Neoglaciación', durante el cual la incidencia de los incendios naturales (por ejemplo, los incendios inducidos por relámpagos o desprendimientos de rocas) habría sido menor. Esto sugiere que las actividades humanas pudieron desempeñar un papel importante en el régimen de los incendios de este período. Posteriormente, durante la Época Romana e inicios del período Germánico (alrededor del 2000–1500 cal BP), se formó una nivel de suelo con una proporción de BC más alta. La proporción de marcadores de BC disminuye, pero sigue siendo considerable, desde hace ca. 1500 cal BP hasta fechas más recientes (no existen dataciones más recientes).

Estos resultados demuestran el impacto del fuego en las propiedades químicas de la MOS. La cronología identificada encaja bien con el régimen de incendios

antrópicos en otras zonas de altitud media en Europa Occidental y Central: aceleración de la erosión y deforestación relacionada con el cambio hacia una sociedad sedentaria y agraria en el Neolítico, seguido por un largo período de incendios frecuentes (aunque su número no se puede calcular con exactitud utilizando registros coluviales). Por lo tanto, el paisaje vegetal de *o monte* en el NO Peninsular, dominado por matorral, y el manejo asociado (tala y quema, rozas, etc.), tiene sus raíces en los incendios de la prehistoria, por lo menos en parte provocados por las sociedades del pasado.

II. Identificación y caracterización molecular del *Black Carbon* antiguo: Estudios metodológicos

Los Manuscritos 4, 5 y 6 presentan estudios metodológicos cuyo objetivo es identificar, caracterizar y cuantificar el BC antiguo. Se consideró necesario ampliar la batería de métodos aplicada a los suelos de PRD-1 y PRD-2 para apoyar las interpretaciones dadas en los Manuscritos 1–3, que fueron consideradas como especulativas debido a los problemas en la identificación del BC antiguo en muestras complejas como la MOS, por investigadores sin experiencia sólida en pirólisis-CG/EM.

Muestras seleccionadas de carbón macroscópico y MOS de extractos de NaOH fueron sometidas a una serie de métodos avanzados de caracterización molecular para estudiar las propiedades químicas. Se eligieron métodos que se aplican, a menudo, en el campo de investigación del BC, y la pirólisis analítica para establecer su complementariedad con estos métodos (**Manuscrito 4**): pirólisis-CG/EM, termoquimiólisis-CG/EM, dos tipos de RMN de sólidos (polarización cruzada y polarización directa; PC y PD RMN), y el análisis de formas policarboxílicas de benceno (método BPCA). Según los resultados PD-RMN (el método más fiable a nivel cuantitativo) la MOS extraíble en NaOH consiste de 30–50 % BC. El método BPCA proporciona valores más bajos, probablemente porque con el BPCA se analizan los núcleos poliaromáticos grandes, mientras que estructuras de menos de tres anillos aromáticos fusionados se escapan del alcance del método (según el mecanismo propuesto por Ziolkowski and Druffel, 2009). Así, un grado de condensación aromática bajo, puede explicar la discrepancia entre los resultados de PD RMN y los de BPCA. Por su parte, el bajo grado de condensación es consecuencia de la degradación abiótica y/o biológica que ocurren en el suelo (pos-deposicional), como la oxidación (principalmente, carboxilación) y la despolimerización. Efectivamente, todos los isómeros de bencenos con 1–6 grupos carboxílicos fueron detectados en los cromatogramas de la termoquimiólisis de la MOS extraíble en NaOH, afirmando la presencia de BC fuertemente oxidado en la

MOS. Los resultados señalaron que, por lo menos, el 30–40 % de la MOS extraíble deriva de residuos de paleoincendios. De acuerdo con esto, los suelos de Campo Lameiro están entre los más ricos en BC del mundo.

En el **Manuscrito 5** se intenta hacer una cuantificación de la proporción de MOS pirogénica en la fracción amorfa, es decir, cuantificar el BC que no forma parte de carbones macroscópicos o microscópicos con su estructura esencialmente intacta, mediante el análisis de láminas delgadas de suelo intacto. Al mismo tiempo, con este estudio se pretendía reunir más evidencias, sobre la excepcional abundancia de BC en estos suelos, y obtener información sobre la naturaleza y organización de los componentes del suelo (orgánicos e inorgánicos) que, en muchos casos, reflejan procesos de pedogénesis. Desafortunadamente, el análisis automático, informatizado, de las imágenes obtenidas de las láminas delgadas no permitió la cuantificación de la fracción más oscura de la MOS amorfa que deriva, en parte, del BC. La causa se debe, no sólo, a la presencia de algunos minerales que dieron píxeles tan oscuros como la propia MOS pirogénica, sino que, además, una parte del BC proporcionaba intensidades de píxel relativamente altas (es decir, píxeles menos oscuros, en el rango más oscuro de la MOS no-pirogénica) como resultado del efecto de reflexión de la luz en los poros y bordes de las partículas de BC. Con todo, no se podía evitar este efecto bajando la intensidad de la luz trasmitida, ya que no permitía distinguir entre las diferentes fotoclases de la MOS en los histogramas de las imágenes. Sin embargo, el estudio micromorfológico de los suelos PRD (PRD -1, -2, -4 y -5) sirvió para (1) afirmar la abundancia de BC en una multitud de tamaños y formas, y (2) identificar la degradación biológica del BC en los excrementos de animales xilófagos en fragmentos de carbón vegetal (en aquel momento muchos autores consideraban que el carbón vegetal tiene una recalcitrancia casi ilimitada frente a la degradación, es decir, era ‘inerte’) y, por último, (3) reconocer el proceso de incorporación del BC en la fracción fina del suelo: se detectaron agregados de MOS oscura y amorfa dentro de fragmentos de carbón, y esta MOS formaba la matriz microgranular de los suelos. Por primera vez, se demostró que la degradación biológica del BC promueve la conversión de BC reconocible morfológicamente hacia partículas amorfas ligadas a la fracción mineral y la fracción no-pirogénica de las MOS. Este proceso puede explicar la discrepancia entre la cantidad y concentración de carbón macroscópico y la huella molecular de la MOS (véase Manuscrito 2). Finalmente, la presencia de esclerocios –por ejemplo Manuscrito 4/Figura 1b, y Manuscrito 5/Figura 4a– que, probablemente procedan del hongo *Cenococcum geophilum*, nos obliga a concluir que este hongo que se observa en ambientes enriquecidos en carbón (principalmente en yacimientos arqueológicos; ver Alonso y López, 2005) puede haber tenido un papel primordial en la descomposición de la MOS, incluso, la del BC.

También se estudió la carbonización artificial durante la fase de pirólisis con el objetivo de establecer condiciones óptimas para el estudio del BC con pirólisis-CG/EM, utilizando un nuevo equipamiento (**Manuscrito 6**). Éste incluía un pirolizador de calentamiento resistivo con un hilo de Pt (Pyroprobe 5000, CDS). Al contrario del pirolizador *Curie-point* que se utilizó en los estudios presentados en los Manuscritos 1, 2 y 3, y la gran mayoría de los estudios previos de BC, este equipo permite variar la temperatura de pirólisis (300–1400 ºC). Con el objetivo de comparar la conducta pirolítica del BC y de la de materia no-pirogénica, se utilizó una muestra de la turbera *Pena da Cadela* (NO Peninsular), y un fragmento de carbón antiguo de Campo Lameiro. Estas muestras fueron pirolizadas a temperaturas entre 400 y 1200 ºC para así monitorizar la carbonización artificial de la muestra de turba (en la cámara de pirólisis), y examinar los cambios en la huella molecular del carbón. A una temperatura de 750 ºC la carbonización artificial de la turba es limitada, mientras que la pirólisis del BC (el fragmento de carbón) es efectiva para producir cromatogramas de alta calidad y, por lo tanto, se consideró que ésta era la temperatura más adecuada para el estudio del BC. Además, se aplicó este método a 91 fragmentos de carbón macroscópico del suelo coluvial PRD-4 de Campo Lameiro. Este suelo contiene carbón vegetal reciente de hasta > 11.000 años de antigüedad, lo que permite estudiar los cambios en la señal pirolítica con la edad del BC. Previo al análisis, se identificó el origen botánico del carbón de este suelo aplicando la metodología antracológica. Para ello, se seleccionaron fragmentos de abedul (*Betula* sp.), roble caducifolio (*Quercus* sp.), y leguminosas (Fabáceas).

De una muestra determinada, los fragmentos de carbón vegetal de estos especies (supuestamente, fragmentos de la misma edad) produjeron cromatogramas sorprendentemente similares. Sin embargo, se observaron grandes diferencias en términos de edad. El carbón reciente contenía una proporción significativa de grupos químicos típicos de la materia orgánica ligeramente o no-carbonizada, mientras que el carbón antiguo producía, exclusivamente, marcadores de materia orgánica fuertemente alterada por el impacto térmico. De uno o de otro modo, parece que la pirolizabilidad del BC aumenta progresivamente con la edad. Ello se puede atribuir a la gradual despolimerización del carbón altamente condensado. Asimismo, el método optimizado permitió la identificación de una serie de productos de pirólisis que contienen nitrógeno que hasta entonces no se habían detectado en muestras de BC de origen vegetal, como el C_1-benzoxazola, dicarbonitrilos de benceno, 2-fenilpiridina, naftaleno carbonitrilo y 2-bifenil carbonitrilo, más tarde confirmados por las investigaciones de Song y Peng (2010).

III. Sobre la historia del fuego en Campo Lameiro

El impacto térmico de la quema elimina diferencias en la composición química de las plantas. Por lo tanto, las técnicas de pirólisis tienen una capacidad limitada para investigar el origen botánico del carbón vegetal. Esta limitación de la caracterización molecular del BC implica que son necesarias otras metodologías para desarrollar las líneas de investigación sobre la historia del fuego, especialmente las relaciones entre los cambios de la vegetación, el clima y las actividades humanas a lo largo del Holoceno.

Se determinó el origen botánico del polen (palinología) y del carbón vegetal (antracología) procedentes del suelo PRD-2 para estudiar la reciprocidad entre los cambios en la vegetación y el régimen de incendios de los últimos ca. 6300 años (**Manuscrito 7**). Los resultados indicaron que hasta aproximadamente el 6000–5500 cal BP la vegetación fue un bosque abierto de roble caducifolio (*Quercus* cf. *Q. robur*), en un hábitat con herbáceas, helechos y abundantes arbustos en el sotobosque. En estas fechas, se produjo una perturbación en la vegetación leñosa causada, probablemente, por los incendios. Ampliando las informaciones al respecto, se puede añadir que las comunidades de arbustos sustituyeron a una parte considerable del robledal. Otras fases de degradación del bosque abierto de roble y la expansión de arbustos, tipo Fábaceas leñosas y/o *Erica* cf *E. arborea*, sucedieron aproximadamente en el 4000–3500 cal BP y alrededor del 2500 cal BP. Las especies de brezo fueron dominantes en los registros de polen y carbón desde el ca. 1700 cal BP, momento en el que se formó una capa de suelo enriquecida en carbón vegetal macroscópico (hasta 10 mg de carbón por g de tierra fina). Por otro lado, la concurrencia de la acumulación de carbón vegetal y la expansión del brezal, confirma la estrecha relación entre los incendios y el retroceso del bosque. Por encima de esta capa de suelo, datada alrededor del 1700 cal BP, la concentración del carbón macroscópico se reduce gradualmente aunque no coincide con una recuperación local del bosque. Efectivamente, después del ca. 1700 cal BP se formó un brezal maduro, tal como sugiere la disminución en el grado de curvatura de los anillos del carbón vegetal.

En general, estos cambios en la vegetación fueron más acentuados en el registro del carbón que en el de polen, probablemente, porque este último es fácilmente transportado por el viento, mientras que el carbón y, particularmente, el carbón macroscópico (> 2 mm), el que se ha utilizado en este estudio, no recorre distancias significativas. Precisamente, el registro de polen tiene un carácter mucho más regional que el registro de carbón macroscópico. La presencia de polen de alisos y otros especies riparias y su total ausencia en el registro de carbones refuerza esta interpretación. Un cambio en la vegetación local, con pocos efectos en la ubicada a menor elevación (valle y laderas bajas) del Monte Paradela, podría haber generado

un efecto significativo en la composición botánica del carbón mientras que no se detectaría en el registro polínico. Otra discrepancia importante entre los registros de polen y carbón es la profusión de carbón derivado de Fabáceas (especies de tojo y retama), escasamente representados en el polen. La causa más probable de esta discrepancia es la intensa corrosión y casi completa descomposición del polen de estas especies en el Ranker Atlántico (según van Mourik, 1986). Aparte de los incendios, otro factor detectado en todas las capas de suelo de edades desde el 6000 cal BP hasta fechas recientes, fue el pastoreo local, evidenciado por la omnipresencia de especies indicadoras de espacios antropizados, i.e. 'sinantrópicas', y nitrófilas, como la ortiga (*Urtica dioica*) y el llantén (*Plantago lanceolata*), en el polen. En resumen, este estudio demostró que la deforestación de la zona era más intensa en las partes altas que en las zonas del valle y las laderas inferiores, dónde la vegetación arbórea (*Betula* sp., *Quercus* sp. y *Alnus* sp.) siguió siendo más profusa. Por lo tanto, los incendios y el pastoreo debieron haber tenido un carácter local, en las partes superiores de las laderas. Laderas y sierras deforestadas (*o monte*), cubiertas por suelos coluviales oscuros, son ubicuas en el NO Peninsular. Estas zonas frecuentemente están rodeadas por laderas inferiores y valles con una vegetación arbórea más desarrollada. Se propone que esta dualidad del paisaje, todavía bien visible en la actualidad, se creó ya en épocas prehistóricas y que las sociedades del pasado tuvieron un papel importante en este proceso.

Aumentando la resolución (en número de muestras por época) y el rango cubierto por los registros (los últimos ca. 13.000 años en vez de ca. 6000 años de PRD-2), el estudio antracológico de los cinco suelos PRD facilitó una elaboración más detallada de la reconstrucción de la historia del fuego en Campo Lameiro (**Manuscrito 8**). La vegetación leñosa del Holoceno temprano (ca. 13.000–11.000 cal BP) estaba formada principalmente por *Betula* sp. (abedul), arbustos (tipos Fabáceas) y, seguramente, una gran variedad de especies herbáceas. Este paisaje vegetal abierto fue colonizado por el roble caducifolio, probablemente *Quercus robur*, formando así un bosque bien desarrollado a partir del 10.000 cal BP hasta aproximadamente el 5500 cal BP. Sin embargo, alrededor del 7000–6500 cal BP tuvo lugar una fase de regresión del bosque (roble) y expansión de arbustos (principalmente madroño, i.e. *Arbutus unedo*), lo que puede reflejar el inicio del uso del fuego por el hombre, con el objetivo más probable de crear espacios abiertos para las prácticas de caza (este evento sucede en un contexto pre-agropastoral). Una perturbación más radical ocurrió alrededor del 5500 cal BP. La regresión del roble, desde más de 60 % a menos de 30 % del carbón, coincidió con un incremento de la concentración de carbón macroscópico, sugiriendo una relación estricta entre la intensidad del régimen de los incendios y el equilibrio bosque-matorral. Otras fases de degradación ambiental acelerada (deforestación, erosión, acidificación) ocurrieron ca. 4000–3500 cal BP, 3000–2000 cal BP y 2000–1500 cal BP. El roble se recuperó parcialmente

después de estas fases, excepto la última de ellas que corresponde a la Época Romana/Germánica, durante cuál se formó un brezal maduro que en los registros de carbones continua hasta las fechas más recientes estudiadas.

El único suelo en el que no se detectaron estas fases, con la excepción de la última ca. 1500 cal BP, fue PRD-4. Este suelo está situado a la menor altitud de los estudiados. Su registro de carbón sugiere que la disminución de la cobertura del robledal se inició varios milenios más tarde que en otras áreas de Paredes. Estos resultados son coherentes con la señal local de la deforestación por incendios, concentrado en las laderas superiores de la zona estudiada (Manuscrito 7).

Algunas de las fases de expansión de las comunidades arbustivas (matorral), y *Erica* sp. en particular, coinciden con períodos reconocidos como fases de deforestación acelerada e impacto humano en el NO Peninsular y Europa en general. Especialmente, la fase del Neolítico (ca. 6000–5500 cal BP) está detectada en muchos registros de Europa Central y Occidental y se atribuye, generalmente, a la intensificación del proceso de adaptación de sistemas agropastorales por las sociedades anteriormente nomádicas. Por otro lado, el evento detectado entre el 3000 cal BP y el 2000 cal BP (Edad de Bronce Final y Edad del Hierro), así como en Época Romana y la transición hacia el período Germánico (el evento a ca. 2000–1500 cal BP), son épocas en que la población y su impacto al paisaje (p. ej. a través de la actividad minera) creció significativamente. Es interesante constatar que algunas de estas fases coinciden con períodos de cambios climáticos rápidos. Esto sugiere que existe una relación entre los cambios ambientales y cambios en la naturaleza, intensidad y/o en impacto de las actividades humanas. Estos resultados, junto a la evidencia del impacto del pastoreo (Manuscrito 7) sugieren que las fases de cambios en la vegetación posterior al ca. 6000 cal BP fueron inducidos por los incendios antrópicos, cuyo objeto podría haber sido el acondicionamiento de la zona para el pastoreo. Los incendios recurrentes inhibieron la recuperación del bosque caducifolio a escala local. Por lo tanto, el 'paisaje del fuego' y la 'cultura del fuego', hoy en día bien identificables en *o monte* gallego, tienen sus raíces, como se afirmó anteriormente, en las prácticas de tala y quema o sistemas parecidos que incluyen el aclarado de bosque aplicando el fuego y el posterior mantenimiento del pasto. En el área del Parque Arqueológico del Arte Rupestre se aplicó el fuego con esta finalidad desde hace, por lo menos, 6000–5500 años.

IV. Síntesis

Los hallazgos principales de estos estudios son, en primer lugar, que los Ránkeres Atlánticos contienen grandes cantidades de residuos de fuego (BC). En segundo lugar, que la gran mayoría de este BC reside en el suelo en compuestos amorfos, oxidados, despolimerizados y mezclados con la MOS no-pirogénica y con

la fracción mineral en los micro-agregados del suelo. Anteriormente, no se consideraba que la MOS que tiene estas características fuese un producto del BC. En tercer lugar, el particular comportamiento de la MOS y el color oscuro/negro del Ranker Atlántico se deben en parte al efecto de ennegrecimiento del BC y, por lo tanto, está relacionado de forma directa con los paleoincendios. Se concluye que el papel del fuego en la pedogénesis del Ranker Atlántico estaba previamente subestimado. En cuarto lugar, se demostró que el BC se acumuló en las depresiones del Monte Paradela como consecuencia de un intenso régimen de incendios locales, los cuales habrían inhibido la regeneración del bosque caducifolio y facilitado la expansión de los arbustos que, finalmente, formaron un matorral de brezo denso y prácticamente desarbolado. En quinto lugar, los incendios fueron un factor principal en la deforestación prehistórica de *o monte* en el NO Peninsular, que se inició ca. 7000–6500 cal BP y aceleró en varias fases posteriores (ca. 5700–5300 cal BP, 4000–3500 cal BP, 3000–2000 cal BP y 2000–1500 cal BP). Cabe destacar que en la época de la creación de los petroglifos, el paisaje ya estaba fuertemente deforestado. Finalmente, parece que los incendios fueron principalmente antrópicos. Por lo tanto, la deforestación de *o monte*, la expansión de matorral bien adaptado a los incendios (en este ecosistema), y la erosión de la zona, fueron iniciados por sociedades prehistóricas.

RESUMO

O Centro de Interpretación e Documentación da Arte Rupestre (CIDAR)[3] en Campo Lameiro (Pontevedra, Galicia, NO Peninsular) está destinado a ser un lugar de visita para turistas e expertos na materia, así como sede de exposición, divulgación e protección do patrimonio arqueolóxico, e desempeñar labores de investigación científica e técnica. Este centro, que probablemente será inaugurado a finais do ano 2010, está rodeado por gravados de arte rupestre (petróglifos), formando o nomeado Parque Arqueolóxico de Arte Rupestre de Campo Lameiro. Cabe apuntar que os petróglifos se crearon, aproximadamente, entre hai 4500 e 2500 anos antes do presente (cal BP). Como consecuencia da escaseza de artefactos arqueolóxicos nas escavacións, descoñécense as actividades das sociedades, o que crea un escenario de incerteza sobre a cronoloxía e a función da cultura rupestre.

A cobertura edáfica do Parque Arqueolóxico de Arte Rupestre son maioritariamente solos coluviais de intensa cor negra, algúns de gran potencia (> 1 m de grosor). A estes solos denomináselles Ranker Atlántico e fórmanse a través da erosión/sedimentación desde inicios do Holoceno. Polo tanto, son arquivos que conteñen un rexistro físico dos cambios ambientais. No ano 2003 tomáronse columnas de solo para a súa análise co fin de xerar coñecemento paleoambiental (estabilidade xeomorfolóxica do solo, exhumación de rochas, cambios nas condicións climáticas, acidificación, etc.) e déuselle gran relevancia aos sinais xeoquímicas das fases inorgánicas. Hai que apuntar, neste sentido, que inicialmente os estudos da materia orgánica limitáronse, de xeito máis preciso, á análise elemental e ás extraccións selectivas. Foi no ano 2005 cando se iniciou un estudo cuxo obxectivo era proporcionar información arqueolóxica e paleoambiental aplicando unha metodoloxía avanzada para o estudo da composición molecular da materia orgánica do solo (MOS). Este estudo é o obxectivo desta tese. Unha circunstancia que hai que matizar é que ata entón non se levara a cabo ningunha caracterización molecular da MOS típica do Ranker Atlántico.

No que segue, e de maneira breve, comentaremos que as análises moleculares da MOS demostraron que os solos do Parque Arqueolóxico de Arte Rupestre conteñen cantidades considerables de residuos de lume (*Black Carbon*, BC) en todos os niveis. Estes resultados apuntan a que o lume xogou un papel importante na historia da zona estudada. A identificación, a caracterización molecular e o significado deste BC forman o corpo desta tese, contido que resumiremos e explicaremos a continuación.

[3] Proxecto adscrito á Consellaría de Cultura, Comunicación Social e Turismo, e que conforma a Rede Galega de Patrimonio Arqueolóxico (RGPA), canda o parque do mundo romano de Lugo, o parque da cultura castrexa en San Cibrán de Las (Ourense) e o parque de megalitismo da Costa da Morte (A Coruña).

I. *Black Carbon* nos solos coluviais do NO Peninsular

Unha proporción significativa da materia orgánica do solo (MOS) acumulada no solo PRD-1 do Parque Arqueolóxico de Arte Rupestre de Campo Lameiro é de orixe piroxénica (**Manuscrito 1**). Esta conclusión explícase pola proporción excepcionalmente alta de produtos de pirólise que se atribúen, habitualmente ao BC, tales coma os bencenos e os hidrocarburos aromáticos policíclicos (HAPs). As resonancias dominantes de átomos ^{13}C de grupos aromáticos nos espectros de Resonancia Magnética Nuclear (RMN) en estado sólido, confirmaron a abundancia de BC. A proporción dos 'indicadores moleculares de BC' é independente do contido en carbón macroscópico (> 2 mm). Esta afirmación tentativa susténtase nos estudos metodolóxicos de pirólise presentados nos Manuscritos 4–6. Consecuentemente, a abundancia de BC en extractos de sosa (NaOH (aq)) é moito maior que a de BC en carbón macroscópico. Estes resultados revelan que os incendios ocorreron de forma habitual durante os últimos 8000 anos. Non se detectaron marcadores químicos de vexetación específica do pasado, nin residuos de fauna, nin artefactos de actividade humana (excepto, talvez, o lume), feito que se pode atribuír á degradación térmica pre-deposicional (lume) e, probablemente máis importante, á degradación biolóxica pos-deposicional.

O **Manuscrito 2** oriéntase ás características químicas da MOS no solo PRD-1, utilizando os dados obtidos mediante pirólise-cromatografía de gases/espectrometría de masas (pirólise-CG/EM) de fragmentos de carbón macroscópico e da MOS extraíble en NaOH. Dada a escasa información dispoñible sobre o comportamento pirolítico do BC, especialmente no caso de BC antigo, analizouse carbón vexetal do mesmo solo para poder extraer, comparativamente, a pegada pirolítica do carbón antigo, e así recoñecer produtos de BC antigo nos extractos de NaOH. Os bencenos, o benzonitrilo, e os HAPs representan un 60–98 % dos pirolisatos (porcentaxe da área cuantificada total, ACT) do carbón macroscópico. Estes produtos de pirólise representan o 21–54 % da ACT da fracción extraíble en NaOH, confirmando deste xeito a abundancia de BC no extracto e, polo tanto, na fracción fina do solo. Consecuentemente, a resistencia fronte á degradación, inherente ao BC, pode explicar a estabilidade da MOS a longo prazo. Ademais do BC, son abundantes os produtos de pirólise da MOS degradada non-piroxénica (derivada de ligninas, proteínas, lípidos e carbohidratos). Non obstante, a alta concentración de óxidos, hidróxidos e oxihidróxidos de Fe e Al, de baixa cristalinidade, protexe o BC oxidado e a MOS non-piroxénica fronte á descomposición biolóxica, debido á súa adsorción a estes compoñentes do solo (mediante enmascaramento de grupos funcionais). A proporción de produtos de pirólise da MOS intacta ou pouco degradada, coma o levoglucosán, derivado da celulosa, e os compostos metoxifenólicos da lignina, é moi baixa na superficie do solo (< 5 % da ACT), e incluso está por debaixo do límite de

detección (ca. 0.2 %) na parte inferior do solo, o que confirma o alto grao de degradación da MOS. Con toda seguridade, a MOS non-piroxénica, que se atopa estabilizada en complexos órgano-minerais, está altamente degradada. O efecto protector do Al e, en menor medida, do Fe pouco-cristalino non lle afecta á MOS fresca (biopolímeros recoñecibles). Cabe inferir que estes resultados representan información nova sobre a xénese dos Ránkeres Atlánticos: a súa formación está rigorosamente relacionada co réxime de paleoincendios. Non se atopou ningunha evidencia de podzolización nos datos de pirólise-CG/EM de PRD-1, en concordancia co estudo xeoquímico do mesmo solo, no que se concluíu que a MOS non sufriu mobilización (Kaal et al., 2008). Este estudo constitúe o primeiro rexistro de paleoincendios baseado na caracterización molecular da MOS.

A interpretación cronolóxica da historia dos incendios e a súa relación coa actividade humana, tal e como revela a pirólise-CG/EM dos solos PRD-1 e PRD-2, descríbese no **Manuscrito 3**. Aplicando análises estatísticas, identificáronse diferenzas na composición da MOS que permitiron establecer oito fases de formación, con propiedades distintas na frecuencia e na intensidade dos incendios. Os primeiros incendios detectados nestes solos son anteriores ao 8500 cal BP. Un incremento na proporción de bencenos e HAPs suxire unha intensificación no réxime de incendios arredor de 8500–6000 cal BP, que corresponde ao Mesolítico/Epipaleolítico e ao Neolítico temperán na cronoloxía arqueolóxica, e ao período húmido e cálido do Máximo Térmico do Holoceno (o 'Hipsitermal') na cronoloxía climatolóxica. Unha variación nas proporcións relativas de bencenos e HAPs ca. 6000 cal BP indica un cambio nas condicións dos incendios e/ou na natureza do combustible. A hipótese máis probable parece ser un cambio na cobertura vexetal, dende unha dominancia arbórea a unha vexetación máis arbustiva (mato). A relativamente rápida sedimentación de material homoxéneo e rico en BC, dende aproximadamente 6000 cal BP ata ca. 2000 cal BP, apunta á existencia dun sistema recorrente de incendios e erosión durante o Neolítico, a Idade do Bronce e a Idade do Ferro. Este período inclúe un episodio climático longo e frío, a 'Neoglaciación', durante o que a incidencia de incendios naturais (por exemplo, os incendios inducidos por relampos ou desprendementos de rochas) sería menor. Isto suxire que as actividades humanas posiblemente tiveron un papel importante no réxime de incendios neste período. Posteriormente, durante a Época Romana e inicios do período Xermánico (arredor do 2000–1500 cal BP), formouse un nivel de solo cunha proporción de BC máis alta. A proporción de marcadores de BC diminúe, aínda que segue sendo considerable, dende ca. 1500 cal BP ata datas máis recentes (que non podemos precisar por carecer de datacións radiocarbónicas).

Estes resultados demostran o impacto do lume nas propiedades químicas da MOS. A cronoloxía identificada encaixa co réxime de incendios antrópicos noutras zonas de altitude media en Europa Occidental e Central: aceleración da erosión e

deforestación relacionada co cambio cara a unha sociedade sedentaria e agraria no Neolítico, seguido dun longo período de incendios frecuentes (aínda que o seu número non se pode calcular con exactitude utilizando rexistros coluviais). Polo tanto, a paisaxe vexetal do monte no NO Peninsular, dominada por mato, e o manexo asociado (tala e queima, rozas, etc.), ten as súas raíces nos incendios da prehistoria, que parecen ser, polo menos en parte, intencionadamente provocados polas sociedades do pasado.

II. Identificación e caracterización molecular do *Black Carbon* antigo: estudos metodolóxicos

Os Manuscritos 4, 5 e 6 presentan estudos metodolóxicos cuxo obxectivo é identificar, caracterizar e cuantificar o BC antigo. Considerouse necesario ampliar a batería de métodos aplicada aos solos do PRD-1 e PRD-2 para apoiar as interpretacións dadas nos Manuscritos 1–3, que foron consideradas como especulativas debido aos problemas na identificación do BC antigo en mostras complexas como a MOS, por investigadores sen experiencia en pirólise-CG/EM.

Mostras seleccionadas de carbón macroscópico e MOS de extractos de NaOH foron sometidas a unha serie de métodos avanzados de caracterización molecular para estudar as propiedades químicas. Elixíronse métodos que se aplican, a miúdo, no campo de investigación do BC, e a pirólise analítica para establecer a súa complementariedade con estes métodos (**Manuscrito 4**): pirólise-CG/EM, termoquimiólise-CG/EM, dous tipos do RMN de sólidos (polarización cruzada e directa; PC e PD RMN), e a análise de formas policarboxílicas de benceno (método BPCA). Segundo os resultados PD-RMN (o método máis fiable a nivel cuantitativo) a MOS extraíble en NaOH consiste de 30–50 % BC. O método BPCA proporciona valores máis baixos, probablemente porque co BPCA analízanse os núcleos poliaromáticos grandes, mentres que estruturas de menos de tres aneis aromáticos fusionados escápanse do alcance do método (segundo o mecanismo proposto por Ziolkowski and Druffel, 2009). Así, un grao de condensación aromática baixo, pode explicar a discrepancia entre os resultados de PD RMN e os de BPCA. Pola súa banda, o baixo grao de condensación é consecuencia da degradación abiótica e/ou biolóxica que ocorren no solo (pos-deposicional), como a oxidación (principalmente carboxilación) e a despolimerización. Efectivamente, todos os isómeros de bencenos con 1–6 grupos carboxílicos foron detectados nos cromatogramas da termoquimiólise da MOS extraíble en NaOH, afirmando a presenza de BC fortemente oxidado na MOS. Os resultados sinalaron que, cando menos, o 30–40 % da MOS extraíble deriva de residuos de paleoincendios. De acordo con isto, os solos de Campo Lameiro están entre os máis ricos en BC do mundo.

No **Manuscrito 5** inténtase facer unha cuantificación da proporción de MOS piroxénica na fracción amorfa, é dicir, cuantificar o BC que non forma parte de carbóns macroscópicos ou microscópicos coa súa estrutura esencialmente intacta, mediante a análise de láminas delgadas de solo intacto. Ao mesmo tempo, con este estudo pretendíase reunir máis evidencias sobre a excepcional abundancia de BC nestes solos, e obter información sobre a natureza e organización dos compoñentes do solo (orgánicos e inorgánicos) que, en moitos casos, reflicten procesos de pedoxénese. Desafortunadamente, a análise automática, informatizada, das imaxes obtidas das láminas delgadas non permitiu a cuantificación da fracción máis escura da MOS amorfa que deriva, en parte, do BC. A causa non só se debe á presenza dalgúns minerais que deron píxeles tan escuros como a propia MOS piroxénica, senón que, ademais, unha parte do BC proporcionaba intensidades de píxel relativamente altas (é dicir, píxeles menos escuros, no rango máis escuro da MOS non-piroxénica) como resultado do efecto de reflexión da luz nos poros e bordes das partículas de BC. Deste xeito, non se podía evitar este efecto baixando a intensidade da luz transmitida, xa que non permitía distinguir entre as diferentes fotoclases da MOS nos histogramas das imaxes. Porén, o estudo micromorfolóxico dos solos PRD (PRD -1, -2, -4, e -5) serviu para (1) afirmar a abundancia de BC nunha multitude de tamaños e formas, e (2) identificar a degradación biolóxica do BC nos excrementos de animais xilófagos en fragmentos de carbón vexetal (naquel momento moitos autores consideraban que o carbón vexetal ten unha recalcitrancia case ilimitada fronte á degradación, é dicir, era 'inerte') e, por último, (3) recoñecer o proceso de incorporación do BC na fracción fina do solo: detectáronse agregados de MOS escura e amorfa dentro de fragmentos de carbón, e esta MOS formaba a matriz microgranular dos solos. Por primeira vez, demostrouse que a degradación biolóxica do BC promove a conversión de BC recoñecible morfoloxicamente cara a partículas amorfas ligadas á fracción mineral e á fracción non-piroxénica das MOS. Este proceso pode explicar a discrepancia entre a cantidade e concentración de carbón macroscópico e a pegada molecular da MOS (véxase o Manuscrito 2). Finalmente, a presenza de esclerocios –por exemplo Manuscrito 4/Figura 1b, e Manuscrito 5/Figura 4a– que, probablemente, procedan do fungo *Cenococcum geophilum*, obríganos a concluír que este fungo que se observa en ambientes enriquecidos en carbón (principalmente en depósitos arqueolóxicos; ver Alonso e López, 2005) pode ter un papel primordial na descomposición da MOS, incluso, a do BC.

Tamén se estudou a carbonización artificial durante a fase de pirólise co obxectivo de establecer condicións óptimas para o estudo do BC con pirólise-CG/EM, utilizando un novo equipamento (**Manuscrito 6**). Este incluía un pirolizador de quentamento resistivo cun fío de Pt (Pyroprobe 5000, CDS). Ao contrario do pirolizador '*Curie-point*' que se empregou nos estudos presentados nos Manuscritos 1, 2, e 3, e a gran maioría dos estudos previos de BC, este equipo permite variar a

temperatura de pirólise (300–1400 ºC). Co obxectivo de comparar a conduta pirolítica do BC e da materia non-piroxénica, utilizouse unha mostra da turbeira Pena da Cadela (NO Peninsular), e un fragmento de carbón antigo de Campo Lameiro. Estas mostras foron pirolizadas a temperaturas entre 400 e 1200 ºC para así monitorizar a carbonización artificial da mostra de turba (na cámara de pirólise), e examinar os cambios na pegada molecular do carbón. A unha temperatura de 750 ºC a carbonización artificial da turba é limitada, mentres que a pirólise do BC (o fragmento de carbón) é efectiva para producir cromatogramas de alta calidade e, polo tanto, considerouse que esta era a temperatura máis axeitada para o estudo do BC. Ademais, aplicóuselle este método a 91 fragmentos de carbón macroscópico do solo coluvial PRD-4 de Campo Lameiro. Este solo contén carbón vexetal recente de ata > 11.000 anos de antigüidade, o que permite estudar os cambios no sinal pirolítica coa idade do BC. Previo á análise, identificouse a orixe botánica do carbón deste solo aplicando a metodoloxía antracolóxica. Para iso, seleccionáronse fragmentos de bidueiro (*Betula* sp.), carballo caducifolio (*Quercus* sp.), e leguminosas (Fabáceas).

Para os fragmentos de carbón vexetal dunha mostra determinada (supostamente fragmentos da mesma idade), estas especies produciron cromatogramas, sorprendentemente, similares. Non obstante, observáronse grandes diferenzas en termos de idade. O carbón recente contiña unha proporción significativa de grupos químicos típicos da materia orgánica lixeiramente ou non-carbonizada, mentres que o carbón antigo producía, exclusivamente, marcadores de materia orgánica fortemente alterada polo impacto térmico. Dun ou doutro xeito, parece que a pirolizabilidade do BC aumenta progresivamente coa idade. Iso pódese atribuír á gradual despolimerización do carbón altamente condensado. Así mesmo, o método optimizado permitiu a identificación dunha serie de produtos de pirólise que conteñen nitróxeno que ata entón non se detectaran en mostras de BC de orixe vexetal, como o C_1-benzoxazola, dicarbonitrilos de benceno, 2-fenilpiridina, naftaleno carbonitrilo e 2-bifenil carbonitrilo, máis tarde confirmados polas investigacións de Song e Peng (2010).

III. Sobre a historia do lume en Campo Lameiro

O impacto térmico da queima elimina diferenzas na composición química das plantas. Polo tanto, as técnicas de pirólise teñen unha capacidade limitada para investigar na orixe botánica do carbón vexetal. Esta limitación da caracterización molecular do BC implica que son necesarias outras metodoloxías para desenvolver as liñas de investigación sobre a historia do lume, especialmente as relacións entre os cambios da vexetación, o clima e as actividades humanas ao longo do Holoceno.

Determinouse a orixe botánica do polen (palinoloxía) e do carbón vexetal (antracoloxía) procedentes do solo PRD-2 para estudar a reciprocidade entre os cambios na vexetación e o réxime de incendios dos últimos ca. 6300 anos (**Manuscrito 7**). Os resultados indicaron que ata aproximadamente o 6000–5500 cal BP a vexetación foi un bosque aberto de carballo caducifolio (*Quercus* cf. *Q. robur*), nun hábitat con herbáceas, fentos e abundantes arbustos no sotobosque. Nestas datas, produciuse unha perturbación na vexetación leñosa causada, probablemente, polos incendios. Ampliando as informacións ao respecto, pódese engadir que as comunidades de arbustos substituíron unha parte considerable das carballeiras. Outras fases de degradación do bosque aberto de carballo e a expansión de arbustos, tipo fabáceas leñosas e/ou *Erica* cf *E. arborea*, que sucederon aproximadamente no 4000–3500 cal BP e arredor do 2500 cal BP. As especies de breixo foron dominantes nos rexistros de polen e carbón dende o ca. 1700 cal BP, momento no que se formou unha capa de solo enriquecida en carbón vexetal macroscópico (ata 10 mg de carbón por g de terra fina). Por outro lado, a concorrencia da acumulación de carbón vexetal e a expansión da breixoeira, confirma a estreita relación entre os incendios e o retroceso do bosque. Por riba desta capa de solo, datada arredor do 1700 cal BP, a concentración do carbón macroscópico redúcese gradualmente, aínda que non coincide cunha recuperación local do bosque. Efectivamente, despois do ca. 1700 cal BP formouse unha breixoeira madura, tal e como suxire a diminución no grao de curvatura dos aneis do carbón vexetal.

En xeral, estes cambios na vexetación foron máis acentuados no rexistro do carbón que no polínico, probablemente, porque este último é facilmente transportado polo vento, mentres que o carbón, particularmente o carbón macroscópico (> 2 mm), que foi o utilizado neste estudo, non recorre distancias significativas. Precisamente, o rexistro de polen ten un carácter moito máis rexional que o rexistro de carbón macroscópico. A presenza de polen de ameneiro e outras especies riparias e a súa total ausencia no rexistro de carbóns reforza esta interpretación. Un cambio na vexetación local, con poucos efectos na localización a menor elevación (val e ladeiras baixas) de Monte Paradela, podería xerar un efecto significativo na composición botánica do carbón, e non se detectaría no rexistro polínico. Outra discrepancia importante entre os rexistros de polen e carbón é a profusión de carbón derivado de fabáceas (especies de toxo e xesta), escasamente representados no polen. A causa máis probable desta discrepancia é a intensa corrosión e case completa descomposición do polen destas especies no Ranker Atlántico (segundo van Mourik, 1986). Á parte dos incendios, outro factor detectado en todas as capas de solo de idades dende 6000 cal BP ata datas recentes, foi o pastoreo local, evidenciado pola omnipresencia de especies indicadoras de espazos antropizados, i.e. ‘sinantrópicas’, e nitrófilas, como a ortiga (*Urtica dioica*) e chantaxe (*Plantago lanceolata*), no polen. En resumo, este estudo demostrou que a deforestación da zona era máis intensa nas partes altas que nas zonas do val e as ladeiras inferiores, onde a vexetación arbórea

(*Betula* sp., *Quercus* sp. e *Alnus* sp.) seguiu sendo máis profusa. Polo tanto, os incendios e o pastoreo deberon ter un carácter local, nas partes superiores das ladeiras. Ladeiras e serras deforestadas (o monte), cubertas por solos coluviais escuros, son ubicuas no NO Peninsular. Estas zonas frecuentemente están rodeadas por ladeiras inferiores e vales cunha vexetación arbórea máis desenvolvida. Proponse que esta dualidade da paisaxe, aínda ben visible na actualidade, creouse xa en épocas prehistóricas e que as sociedades do pasado tiveron un papel importante neste proceso.

Aumentando a resolución (en número de mostras por época) e o rango cuberto polos rexistros (os últimos ca. 13.000 anos en vez de ca. 6000 anos de PRD-2), o estudo antracolóxico dos cinco solos PRD facilitou unha elaboración máis detallada da reconstrución da historia do lume en Campo Lameiro (**Manuscrito 8**). A vexetación leñosa do Holoceno temperán (ca. 13.000–11.000 cal BP) estaba formada principalmente por *Betula* sp. (bidueiro), arbustos (da familia das Fabáceas) e seguramente, unha gran variedade de especies herbáceas. Esta paisaxe vexetal aberta foi colonizada polo carballo caducifolio, probablemente *Quercus robur*, formando así un bosque ben desenvolvido a partir do 10.000 cal BP ata aproximadamente o 5500 cal BP. Porén, ao redor do 7000–6500 cal BP tivo lugar unha fase de regresión do bosque (carballo) e expansión de arbustos (principalmente érbedo, i.e. *Arbutus unedo*), o que pode reflectir o comezo do uso do lume polo ser humano, co obxectivo máis probable de crear espazos abertos para as prácticas de caza (este evento sucede nun contexto pre-agropastoral). Unha perturbación máis radical sucedeu ao redor do 5500 cal BP. A regresión do carballo, dende máis do 60% a menos do 30% do carbón, coincide cun incremento da concentración do carbón macroscópico, o que suxire unha relación estrita entre a intensidade do réxime dos incendios e o equilibrio bosque-mato. Outras fases de degradación ambiental acelerada (deforestación, erosión, acidificación) sucederon ca. 4000–3500 cal BP, 3000–2000 cal BP e 2000–1500 cal BP. O carballo recuperouse parcialmente despois destas fases, excepto a última delas que corresponde á Época Romana/Xermánica, durante a que se formou unha breixoeira madura que nos rexistros de carbóns continúa ata as datas máis recentes estudadas.

O único solo no que non se detectaron estas fases, coa excepción da última ca. 1500 cal BP, foi PRD-4. Este é o solo que está situado a menor altitude. O seu rexistro de carbón suxire que a diminución da cobertura da carballeira se iniciou varios milenios máis tarde que noutras áreas de Paredes. Estes resultados son coherentes co sinal local da deforestación por incendios, concentrado nas ladeiras superiores da zona estudada (Manuscrito 7).

Algunhas das fases de expansión das comunidades arbustivas (mato), e *Erica* sp. en particular, coinciden con períodos recoñecidos como fases de deforestación acelerada e impacto humano no NO Peninsular e Europa en xeral. Especialmente, a

fase do Neolítico (ca. 6000–5500 cal BP) está detectada en moitos rexistros de Europa Central e Occidental, e atribúese xeralmente á intensificación do proceso de adaptación de sistemas agropastorais polas sociedades anteriormente nómades. Por outra banda, o evento detectado entre o 3000 cal BP e o 2000 cal BP (Idade do Bronce Final e Idade do Ferro), así como na Época Romana e a transición cara ao período Xermánico (ca. 2000–1500 cal BP), son épocas nas que a poboación e o seu impacto na paisaxe (p. ex. a través da actividade mineira) medraron significativamente. É interesante constatar que algunhas destas fases coinciden con períodos de cambios climáticos rápidos. Isto suxire que existe unha relación entre os cambios ambientais e os cambios na natureza, intensidade e/ou no impacto das actividades humanas.

Estes resultados, xunto coa evidencia do impacto do pastoreo (Manuscrito 7) suxiren que as fases de cambio na vexetación posterior ao ca. 6000 cal BP foron inducidas polos incendios antrópicos, no que o obxecto podería ser o acondicionamento da zona para o pastoreo. Os incendios recorrentes inhibiron a recuperación do bosque caducifolio a escala local. Polo tanto, a 'paisaxe do lume' e a 'cultura do lume', hoxe en día ben identificables no monte galego, teñen as súas raíces, como se afirmou anteriormente, nas prácticas de tala e queima ou sistemas semellantes que inclúen o aclarado do bosque aplicando o lume e o posterior mantemento do pasto. Na área do Parque Arqueolóxico de Arte Rupestre aplicouse o lume con esta finalidade dende hai, polo menos, 6000–5500 anos.

IV. Síntese

Os achados principais destes estudos son, en primeiro lugar, que os Ránkeres Atlánticos conteñen grandes cantidades de residuos de lume (BC). En segundo lugar, que a gran maioría deste BC reside no solo en compostos amorfos, oxidados, despolimerizados e mesturados coa MOS non-piroxénica e coa fracción mineral nos micro-agregados do solo. Anteriormente, non se consideraba que a MOS que ten estas características fose un produto do BC. En terceiro lugar, o particular comportamento da MOS e a cor escura/negra do Ranker Atlántico débense en parte para ese fin de ennegrecemento do BC e, polo tanto, está relacionado de forma directa cos paleoincendios. Conclúese que o papel do lume na pedoxénese do Ranker Atlántico estaba previamente subestimado. En cuarto lugar, demostrouse que o BC acumulouse nas depresións do Monte Paradela como consecuencia dun intenso réxime de incendios locais, os cales inhibirían a rexeneración do bosque caducifolio e facilitou a expansión dos arbustos que, finalmente, formaron un mato de breixo denso e practicamente desarborado. En quinto lugar, os incendios foron un factor principal na deforestación prehistórica do monte no NO Peninsular, que se iniciou ca. 7000–6500 cal BP e acelerou en varias fases posteriores (ca. 5700–5300 cal BP,

4000–3500 cal BP, 3000–2000 cal BP e 2000–1500 cal BP). Cómpre destacar que na época da creación dos petróglifos, a paisaxe xa estaba fortemente deforestada. Finalmente, parece que os incendios foron principalmente antrópicos. Polo tanto, a deforestación do monte, a expansión de mato ben adaptado aos incendios (neste ecosistema), e a erosión da zona foron iniciados por sociedades prehistóricas.

PART A

CHAPTER 1: GENERAL INTRODUCTION

1. GENERAL INTRODUCTION

1.1 Soil organic matter

1.1.1 The global C cycle

The circulation of carbon through the lithosphere, hydrosphere, atmosphere, biosphere and pedosphere is referred to as the global C cycle (Hedges, 1992). The total global C pool is estimated to be 7.5 x 10^6 Gt (7.5 x 10^{21} g). It is distributed over a set of reservoirs ('pools') that exchange C over a wide range of time scales. The vast majority of the C (> 99.9 %) is stored in slow cycling C pools in the lithosphere, mainly as limestone (6.0 x 10^6 Gt) and kerogen (coal, crude oil, natural gas and organic C in lower grade deposits such as shales and lignite; 1.5 x 10^6 Gt) (Berner, 1989). Smaller quantities of C exist as dissolved carbonates and organic C in the oceans (39,000 Gt), methane clathrates in ocean-floor sediments (11,000 Gt), dead plant and animal remains and microbial biomass in mineral soil (soil organic matter, 1200 Gt) and peat deposits (360 Gt), living vegetation (610 Gt) and greenhouse gases (CO_2, CH_4) in the atmosphere (750 Gt) (Hedges and Oades, 1997). In general, the exchange of C between the oceans, atmosphere, vegetation and soil (OAVS) is much faster than the exchange of lithospheric C (with the exception of fluxes driven by volcanic processes) and therefore the OAVS fluxes regulate the short-term C cycle, control the radiative balance of the Earth and the short-term global climate dynamics. Humans perturbed the global C cycle, essentially by converting slow cycling C into fast cycling C (CO_2) through fossil fuel combustion and cement production (Denman et al., 2007). Even though soil organic matter (SOM) accounts for only a small proportion of the global C budget, SOM constitutes one of the largest fast cycling C pools. As such, it plays an important role in the short-term C circulation (e.g. Post et al., 1982) and therefore global climate dynamics.

1.1.2 SOM chemistry

Soil organic matter is a mixture of the residues of plant, microbial (fungi, actinomycetes and bacteria) and animal (e.g. arthropods and earthworms) origin (Stevenson, 1994; Kögel-Knabner, 2002). In most soils, vascular plants are the main source of SOM that enters through litterfall and roots (Oades, 1993; Naafs, 2004). In the mineral soil, undecayed ('primary') SOM is biologically and/or abiotically degraded and partially transformed into an amorphous, dark-coloured, high molecular weight and more or less biologically refractory fraction of SOM often referred to as humic substances, humus or humified tissue. The underlying humification process was thought to involve a series of abiotic and biological

polymerisation reactions thereby converting plant-, animal- and microbial-derived relatively low molecular weight degradation products into complex 'resynthesised' polymers (in the range of 10^6 Da) (e.g. Schnitzer, 1978; Nierop, 1999). These humic substances are traditionally operationally divided into three groups: humin, humic acids and fulvic acids, based on their solubility behaviour in acidic and alkaline solution (Sposito, 2008). There are some generally accepted differences in molecular structure for these fractions, such as differences in functional group distribution, average molecular weight and relative proportions of biocomponent sources (Saiz-Jiménez and de leeuw, 1986; Stevenson, 1994). However, the application of advanced molecular characterisation techniques to these humic substances fractions demonstrated their intense chemical heterogeneity and lack of diagnostic components within each fraction, showed strong variability between humic substances fractions from different sites (e.g. Buurman et al., 2009) and debunked some of the concepts supporting the polymerisation models (e.g. Burdon, 2001). Consequently, this subdivision is preferentially avoided: SOM is a complex and heterogeneous mixture of organic constituents and any subdivision should be based on molecular properties and not on extraction/precipitation behaviour. The new view is that the building blocks of SOM may be, but are not necessarily so, assembled in supramolecular substances through weak intermolecular forces (dispersion forces, hydrogen bonding), and not covalent bonding (e.g. Piccolo, 2002).

The main components of SOM are polysaccharides, lignin, proteins, lipids, tannins and their partial degradation products (e.g. Saiz-Jiménez and de Leeuw, 1984; Kögel-Knabner et al., 1988; Nierop, 1999; Derenne and Largeau, 2001; Kögel-Knabner, 2002), which are briefly outlined below.

The most abundant biopolymer in nature is the polysaccharide cellulose. Cellulose is the primary constituent of plant cell walls and constitutes ca. 70–75 % of the dry weight of plants (Higuchi, 1997). It consists of β-(1-4)-linked glucose units (> 10,000) which are, especially under aerobic conditions, rapidly hydrolytically cleaved (i.e. depolymerised). Consequently, cellulose is a relatively easily degradable component and its contribution to SOM tends to decrease with age (Nierop et al., 2001). Most other polysaccharides (e.g. starch, glycogen, hemicelluloses) are easily degraded in the soil environment as well, with the notable exception of the N-containing polysaccharide chitin (a polymer of *N*-acetylglucosamine), which is a major component of fungal cell walls and arthropod exoskeleta (Bierstedt et al., 1998). Chitin, which is the third most abundant biopolymer, occurs in intimate association with proteins (Stankiewicz et al., 1998). Specific preservation mechanims may facilitate the accumulation of microbial carbohydrates, including chitin, in the SOM of some soils such as allophonic Andosols (e.g. Nierop et al., 2005), where these biochemically labile substances are protected against complete mineralisation by sorptive protection and/or by physical occlusion (Buurman et al., 2007).

Lignin is the second most abundant biopolymer. It occurs in plant cell walls and forms a major constituent of wood. Lignin is composed of *p*-hydroxyphenyl, guaiacyl and syringyl subunits linked mainly through β-O-4 bonds on the C_3-aliphatic side-chain, thereby forming a complex three-dimensional polyphenolic network. The lignin composition of SOM provides important clues on the degradation state (degree of C_3-side-chain oxidation) and source material (grass lignin, coniferous/softwood lignin and angiosperm/hardwood lignin can be distinguished from the proportions of *p*-hydroxyphenyl, guaiacyl and syringyl subunits) (Filley et al., 2006). Lignin degradation, which is an oxidative process, depends mainly on fungal activity, and only white-rot fungi are capable of decomposing lignin completely (Kögel-Knabner, 2002). In peat deposits, lignin contribution tends to increase with depth, as a result of selective depletion of other biocomponents such as carbohydrates, although in a more evolved state the contribution may decrease relative to alkyl C from lipids (Buurman et al., 2006). Even though lignin undergoes significant degradation in soils where sufficient oxygen is available, the aromatic moieties in lignin form a major source of aromatic nuclei in SOM (Chefetz et al., 2002).

Polypeptides of amino acids, or proteins, are by far the most important source of N-containing moieties in SOM (Derenne and Largeau, 2001), although, as aforementioned, the accumulation of chitin-derived SOM may contribute significantly to the organic N component in some soils. The diverse chemical build-up (amino acid sequence), molecular conformation (secondary and tertiary structure) and functions (enzymes, storage proteins, structural proteins, etc.) of proteins need no further elaboration here. Although peptide linkages are, similar to polysaccharides, readily broken down in most soil environments, amide groups may still be abundant in highly evolved SOM, in addition to heterocyclic N functionalities (Knicker et al., 1996; Derenne et al., 1998). With an increasing impact of SOM degradation, recalcitrant N containing compounds, originating from microbial biomass but also refractory plant peptides, may accumulate in the fine fraction of soils causing a decline in the C/N ratio, which is often used as an indicator of the degree of humification (Tan, 1993).

Lipids *sensu lato* include fatty acids, suberin, cutin, suberan, cutan, sterols, prenols, and their conjugates. The chain length of plant-derived fatty acids is mainly C_{12}–C_{22} with a strong even-over-odd predominance. Upon microbial degradation, odd-numbered and short-chain fatty acids show a relative increase. In many soils, aliphatic compounds accumulate with age, which is generally attributed to their relative resistance against biodegradation (Baldock et al., 1997) or gradual neoformation of aliphatic geopolymers (de Leeuw et al., 2006). Steroids, hopanoids and other prenol lipids are readily degraded under aerobic conditions but not under anaerobic conditions such as in peat deposits (Schellekens et al., 2009). The biopolyesters cutin (concentrated in plant cuticles) and suberin (concentrated in roots and bark), and their non-hydrolysable analogues cutan and suberan, also form major

sources of the lipids in SOM (Nip et al., 1986; Tegelaar et al., 1995; Kolattukudy, 2001; Nierop, 2001).

Tannins are 'complex polyphenols' with the ability to precipitate proteins (Hättenschwiler and Vitousek, 2000; Appel et al., 2001). Plant-derived tannins are subdivided in two classes, namely condensed tannins (from gymnosperms and angiosperms) and hydrolysable tannins (from angiosperms only). Condensed tannins are oligomers of flavan-3-ol linked through interflavanoid bonds. Hydrolysable tannins are comprised of a central polyol core (usually glucose) esterified to gallic acid or ellagic acid moieties. Tannins are exceptional metal mobilising agents because of the abundance of adjacent hydrolyxic groups on the aromatic rings and their protein binding capacity influences soil nutrient dynamics (Tiarks et al., 1989; Slabbert, 1992; Nierop et al., 2006). Tannin content of vascular plants can be as high as 25 % of dry weight, but the contribution of tannins to SOM is largely unknown because of problems in its detection (Hemingway, 1989; Kraus et al., 2003; Nierop and Verstraten, 2006).

Summarising, SOM is a diverse admixture of organic substances of which the composition is controlled by the source material and the degradation/preservation mechanims that operate on it. Soil parameters that control degradation/preservation mechanisms include pH, moisture content, temperature, texture, soil structure, oxygen availability, redox potential, abundance of sesquioxides, characteristics of the microbial community, and so forth. Finally, pre-depositional processes such as burning further increase the chemical diversity of SOM. Regarding molecular structure, SOM diversity is unlimited.

1.1.3 Black Carbon

Thermal modification of biomass produces a set of inorganic (ash) and organic materials. The organic fraction, collectively referred to as black carbon (BC), consists of weakly charred biomass, charcoal, soot and graphitic black C (Schmidt and Noack, 2000). Virtually all BC that formed in the pre-industrial era, and most post-industrial BC, originates from wildfires. Black C is a versatile type of organic matter, typically having a high specific surface area and resistance against biological degradation. Mainly because of these characteristics, BC is nowadays intensely studied for its potential role in the global C cycle, contaminant immobilisation, soil amelioration and for the opportunity it offers to mitigate C accumulation into the atmosphere (Kuhlbusch and Crutzen, 1995; González-Pérez et al., 2004; Lehmann et al., 2005; Koelmans et al., 2006; Laird, 2008).

Differences in the degree of thermal impact creates a so-called 'BC combustion continuum' which envelopes, with increasing degree of thermal impact, weakly charred biomass, charcoal, soot and graphitic black C (Goldberg, 1985; Hedges et al.,

2000; Masiello, 2004). At the high-temperature end of the combustion continuum, BC consists of a strongly polycondensed (graphitic) aromatic network lacking all thermolabile functional groups present in non-charred biomass. Soot is also a highly condensed aromatic network, but is generated by recondensation of gas-phase decomposition products in a flame and is therefore not a solid residue of the original fuel. On the low temperature end, weakly charred biomass often contains chemical building blocks that reflect the biocomponent from which they originate, such as methoxyphenols in lignin, short-chain *n*-alkanes/*n*-alkenes from lipids and furan-like structures from carbohydrates (Pastorova et a., 1994; Eckmeier and Wiesenberg, 2009; Wiesenberg et al., 2009). Although the average level of thermal impact on charcoal-BC is somewhere in between that of weakly charred biomass and soot/graphitic BC, a charcoal particle can be a heterogeneous mixture of weakly-to-severely charred biomass, trapped combustion products and tar, sometimes comprising an uncharred interior (de la Rosa Arranz, 2007).

From the above it can be deduced that BC may originate from any of the previously mentioned biocomponents that make up SOM (Section 1.1.2). Black C is difficult to distinguish from non-pyrogenic SOM because its predominantly aromatic building blocks occur in many other biocomponents and specific functional groups other than fused aromatics are lacking. Therefore, it is often defined operationally using chemical, thermal and thermochemical oxidation methods (Kuhlbusch and Crutzen, 1995; Gustafsson et al., 2001; Gélinas et al., 2001; Simpson and Hatcher, 2004; Elmquist et al., 2004; Hammes et al., 2007). These methods aim to isolate the BC types through oxidation of non-pyrogenic organic matter. The majority of these methods tend to isolate severe charred and therefore polycondensed BC types (soot and graphitic black C) through harsh oxidation reactions. However, less severely charred material is digested by the oxidation reactions as well, creating an underestimation of BC content. On the other hand, weakly charred BC may survive weaker digestion agents but some non-charred material may do so as well, producing an overestimation of BC content. Hence, due to limitations in their BC detection capacity these methods provide quantitative data of only part of the BC continuum and no universal quantification of BC contribution to soils is achieved (Schmidt and Noack, 2000; Masiello, 2004; Hammes et al., 2007). Other methodological problems of BC arise from artificial charring, mineral matrix effects and interference by non-pyrogenic substances (e.g. de la Rosa Arranz et al., 2009). Identification of BC in soil may be obtained using solid-state ^{13}C Nuclear Magnetic Resonance (NMR) analysis (Knicker et al., 2005a), but the structure elucidation capacity of solid-state ^{13}C NMR is limited. The molecular properties of BC may be assessed from the analysis of benzene polycarboxylic acids (the BPCA method) which provide some information about the degree of charring (Brodowski et al., 2005a, 2007), pyrolysis-GC/MS (de la Rosa Arranz, 2007) or more recently developed techniques such as near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Lehmann et al., 2005),

ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) (Kramer et al., 2004; Hockaday et al., 2006) and solid-state ^{13}C NMR after ^{13}C-enriched benzene sorption (Smernik et al., 2006; McBeath and Smernik, 2009).

Soils that contain significant amounts of BC, mainly from wildfires (natural or anthropogenic), are ubiquitous, but the total amount of BC stored in soils remains unknown (Preston and Schmidt, 2006; and references therein). Hence, the role of BC in the global C cycling has not been quantified. Recent work suggests that, after deposition on and incorporation into soil, BC may be abiotically carboxylated, thereby increasing its solubility, mobility and potential (in terms of accessibility and palatability) to serve as a substrate for the microbial community and soil fauna (Kramer et al., 2004; Cheng et al., 2006; Cohen-Ofri et al., 2006; Bruun et al., 2008). Black C oxidation may render it alkali-soluble and thus form part of humic substances extracts (Haumaier and Zech, 1995). In fact, BC becomes increasingly hard to distinguish from highly aromatic humic acids (Hatcher et al., 1989) through the development of functional groups over time, which explains why identification and quantification of 'aged' BC are difficult tasks (Cohen-Ofri et al., 2006). Many authors suggested that BC may be a source of these so-called Type A humic acids (Shindo, 1991; Haumaier and Zech, 1995; Skjemstad et al., 1996; Golchin et al., 1997; Schmidt et al., 1999; Kramer et al., 2004; Ascough et al., 2011), so that distinction between the two would not be realistic. Therefore, contrary to Sposito (2008), the terms humic substances and BC may not be mutually exclusive.

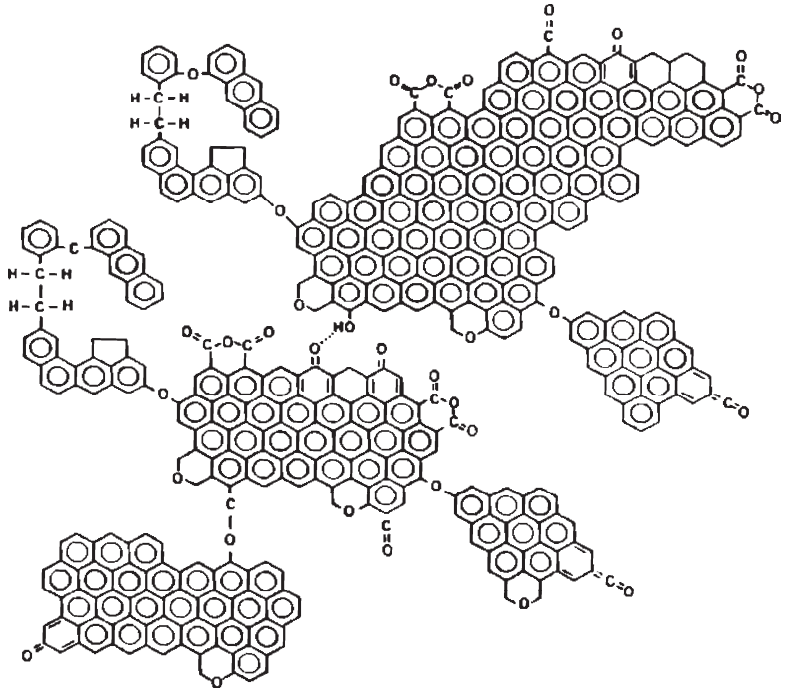


Figure 1.1: The macromolecular model for hexane soot BC proposed by Akhter et al. (1985a/b) and Sergides et al. (1987), later used for BC reviews by Goldberg (1985) and Schmidt and Noack (2000).

Current models of the macromolecular structure of BC (e.g. Figure 1.1) typically assume that relatively large polycondensed aromatic clusters (roughly 15 rings and larger) interconnected through C–C and C–O–C bonds form the molecular backbone of BC (e.g. Goldberg, 1985). This assumption matches reasonably well with experimental and quantum-mechanical modelling data for the macromolecular chemistry of soot, graphite, anthracite coals, carbon nanotubes and other forms of polycondensed aromatics (e.g. Kubicki, 2000; Harris, 2005) but not necessarily with the BC produced during wildfires and especially not with the BC formed upon weak to moderate thermal impact. The knowledge of macromolecular properties of aged BC in terrestrial soil is even more scarce, because the degradation of BC in the natural environment depends on a large array of BC properties (e.g. source material and thermal impact) and soil conditions (hydrology, pH, composition and activity of the microbial population, etc.) that we are only beginning to understand (Baldock and Smernik, 2002; Masiello et al., 2002; Cheng et al., 2006; Czimczik and Masiello, 2007). According to Knicker (2007) and Knicker et al. (2008), the abundance of graphitic sheets of polycondensed aromatic C in BC formed during wildfires has been greatly overestimated in the past. She argues that BC from vegetation fires should be regarded as a heterogeneous mixture of thermally altered biomolecules, consisting of small aromatic clusters (< 6 rings on average) linked predominantly through C–C bonds. The macromolecular model that would emerge from these characteristics is in strong contrast with the models available in literature.

1.2 Methodology

1.2.1 Characterisation of SOM

Natural polymers are too large for direct molecular characterisation. Because the molecular structure of macromolecular organic substances cannot be determined directly (Janoš, 2003), three main approaches have been developed for SOM characterisation. Firstly, a series of analytical techniques facilitate the identification and quantification of functional groups, allowing for a rapid screening of the chemical properties of the SOM. The most frequently employed technique in this category is solid-state ^{13}C NMR. This technique provides information on the distribution of C in functional group classes –or chemical shifts regions: alkyl, methoxyl, *N*-alkyl, *O*-alkyl, di-*O*-alkyl, aryl (aromatic), olefin, *O*-aryl (phenolic), carboxyl, amide and carbonyl– based on differences in resonance energy of ^{13}C nuclei in an artificial electromagnetic field, which depend on the arrangement of the surrounding atoms and groups (Wilson, 1987; Knicker et al., 1996; Kögel-Knabner, 1997; Baldock et al., 2004). It is a routine assessment that cannot be used for detailed molecular characterisation because the structural arrangement of the functional

groups is not revealed. To enhance signal intensity and reduce analysis time, solid-state ^{13}C NMR is often employed in CPMAS (cross-polarisation magic angle spinning) mode. This technique transfers resonance energy from the abundant ^{1}H to the dilute ^{13}C spins (Kögel-Knabner, 1997). Nonetheless, C atoms that are not in close proximity of protons, such as those in polycondensed aromatics, are under-represented by this technique. Therefore, some authors prefer not to apply the CPMAS technique on BC-containing samples and use direct polarisation instead (DP, also known as Bloch-decay). In addition, the CPMAS technique is more sensitive to paramagnetic impurities that cause signal distortion. Solid-state NMR is also used to characterise functional groups containing ^{15}N (Knicker and Lüdemann, 1995) and, more sporadically, ^{1}H and ^{31}P (Wershaw and Mikita, 1987). Other spectroscopic techniques capable of providing qualitative and (semi-)quantitative information on functional groups in SOM are a.o. infra-red (IR) spectroscopy and electron spin resonance (ESR) (Kögel-Knabner, 2000). The second category of SOM characterisation involves isolation of a target fraction of SOM, followed by e.g. gas or liquid chromatography of the isolated material (e.g. lipids extracted by organic solvent; Naafs, 2004). The third category of SOM characterisation uses a degradation process to create lower molecular weight compounds that can then be identified from their mass spectra, often preceded by separation of degradation products by gas chromatography. For example, wet chemolytic degradation methods such as Klason lignin, acid hydrolysis of polysaccharides, amino acid analysis and nitric oxide oxidation of BC can be used to obtain information on specific SOM components (Kögel-Knabner, 2000, 2002; Hatcher et al., 2001). Pyrolytic degradation techniques also belong to this category (see Section 1.2.2).

All these approaches have their advantages and limitations, and none of them supplies unambiguous and/or complete information of SOM composition. Therefore, molecular-level SOM studies preferably involve a combination of methods (Poirier et al., 2005; Templier et al., 2005).

Analytical pyrolysis (pyrolysis-GC/MS) is the most frequently employed technique in this research (Manuscripts 1, 2, 3, 4 and 6). Pyrolysis-GC/MS requires a detailed description because interpretation of results is far from straightforward, especially when BC is present. Brief descriptions of the other methods applied in this thesis can be found in their respective sections of Part B of this thesis: solid-state ^{13}C CPMAS NMR (Manuscript 1, 4), solid-state ^{13}C DP NMR (Manuscript 4), Thermally assisted Hydrolysis and Methylation-GC/MS (THM-GC/MS; Manuscript 4), the BPCA method (Manuscript 4), analysis of thin sections (micromorphology: Manuscript 5), pollen analysis (palynology: Manuscript 7) and charcoal analysis (anthracology: Manuscript 7, 8).

1.2.2 Analytical pyrolysis

Pyrolysis (from Greek-derived pyro=fire and lysis=disintegration) is a molecular degradation process induced by thermal energy in the absence of oxygen or other reagents that may induce or catalyse non-thermal degradation reactions. Thermal impact breaks the weakest bonds in a macromolecule, thereby forming a set of pyrolysis products, which may then recombine or rearrange into secondary pyrolysis products. Depending on the relative stability of bonds within a macromolecule and pyrolysis conditions, the macromolecule breaks apart and produces a set of lower molecular weight GC-amenable pyrolysis products, i.e. the 'pyrolysate' or 'pyrolysis fingerprint' (Wampler, 1999; Leinweber and Schulten, 1999). These pyrolysis products may then be amenable to GC and/or MS analyses.

Pyrolysis-GC/MS is a technique that relies on three hyphenated devices, as shown in Figure 1.2. The solid sample is usually placed in a quartz tube (in resistive heating pyrolysis) or is pressed onto a Curie-point wire (Curie-point pyrolysis), which is respectively rapidly or instantly heated to a predetermined temperature. The thermal energy from the pyrolysis apparatus is transferred to the sample which becomes pyrolysed if the energy is sufficient to break bonds. Typically, pyrolysis of natural biopolymers produces hundreds of different pyrolysis products, so that separation of these compounds is paramount for their identification. Gas chromatography using fused silica columns is the most widely used technique for this

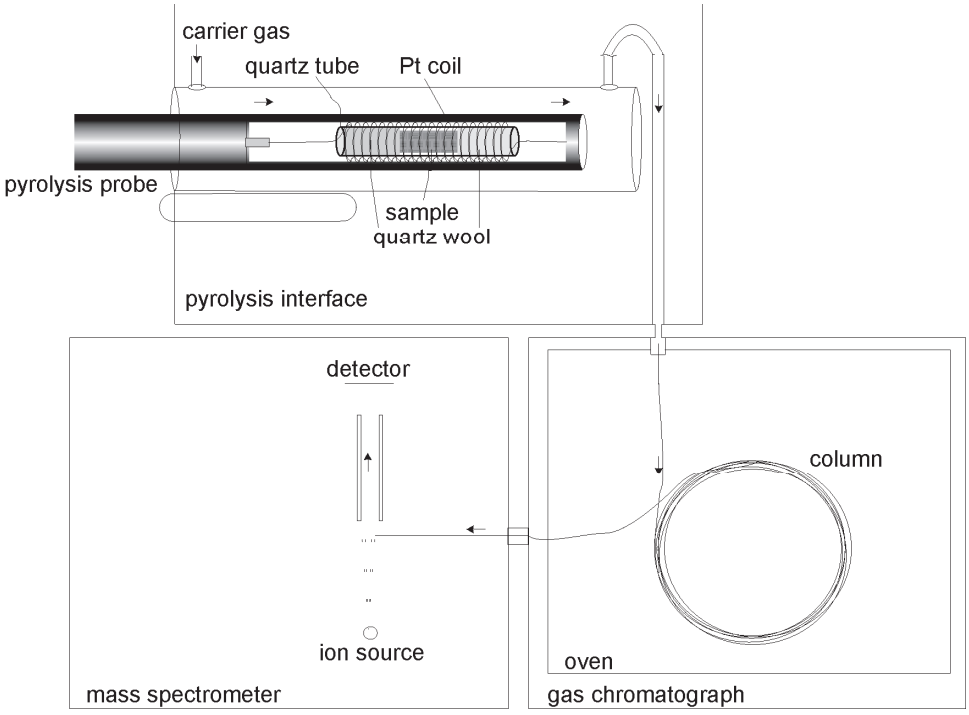
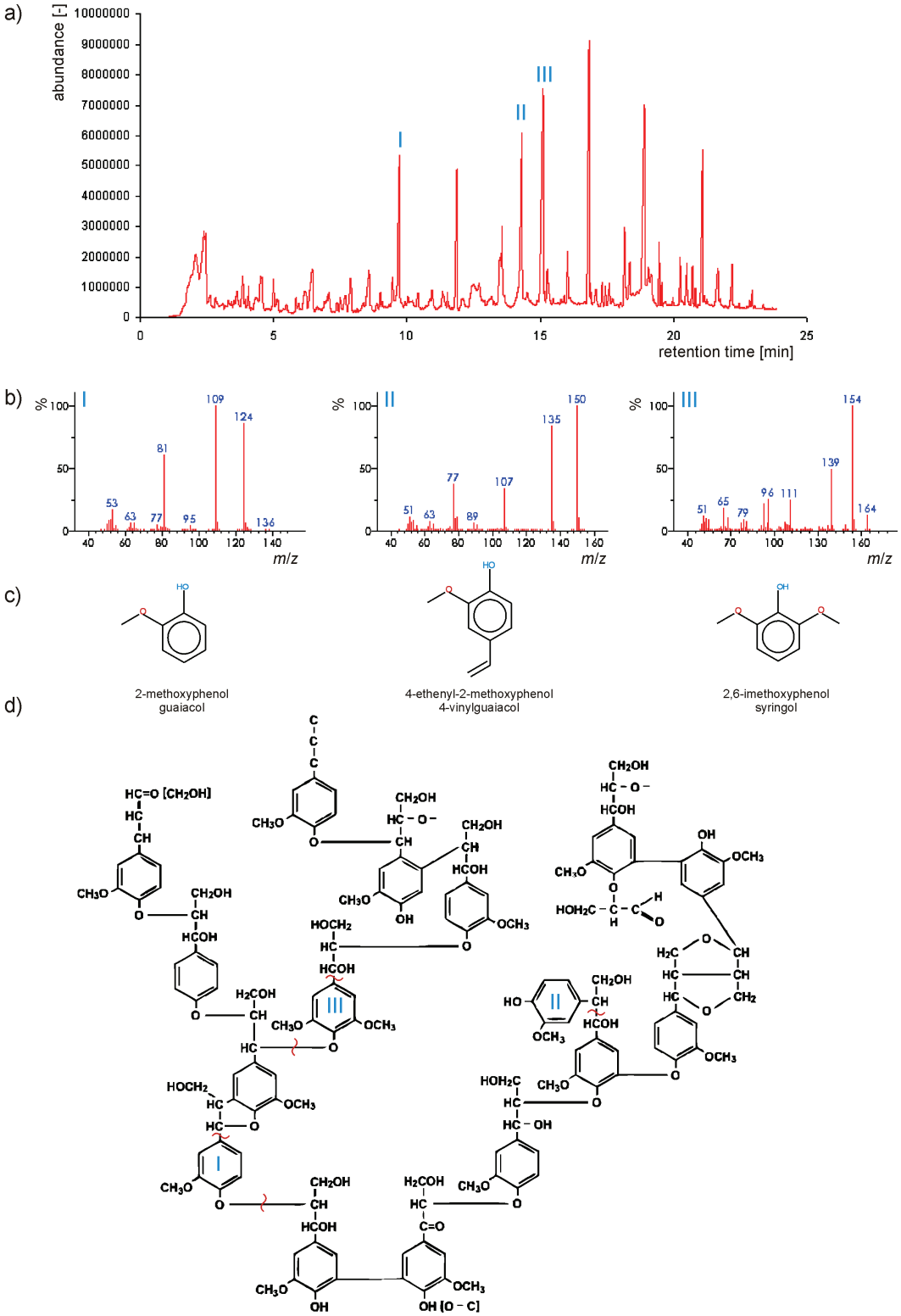


Figure 1.2: Design of an on-line resistive heating heating pyrolysis-GC/MS instrument.

purpose. The pyrolysate is swept from the heated pyrolysis interface by the carrier gas directly into the GC (on-line pyrolysis) or trapped into organic solvent (off-line pyrolysis) and then injected into the GC, where it condensates. The GC oven is then gradually heated thereby volatilising the pyrolysis products as a function of their boiling point and vapor pressure. Pyrolysis products are further separated by the GC column because different products move through it at different rates. The eluting pyrolysis products enter the MS where they become ionised, e.g. by electron impact or chemical ionisation, and may break apart into a pattern of mass fragments that is often specific of the molecule. The charged products are repelled from the ionisation chamber into the electromagnetical fields of a detector where the abundance of mass fragments of specific mass-to-charge ratios (*m*/*z*) is measured. Based on the mass spectral data at a given retention time the pyrolysis products can be identified by comparison with published spectra and mass-spectroscopic libraries. The fragments contained in a pyrolysate can then be translated to (macro)molecular precursors. Figure 1.3 presents an example of pyrolysis-GC/MS of gorse wood.

Figure 1.3 (next page): a) A total ion current chromatogram (or 'pyrogram') obtained from gorse wood (*Ulex europaeus*). The pyrolysate is composed of hundreds of pyrolysis products separated by gas chromatography. b) The mass spectra of selected peaks correspond to methoxyphenolic pyrolysis products: I = guaiacol, II = vinylguaiacol and III = syringol. Guaiacol has a molecular weight of 124 amu. Hence, ionised guaiacol (having lost one electron, i.e. a charge of +1) that is not further fragmented gives *m*/*z* 124 (the molecular ion, or M^+). Elimination of the methoxylic CH_3 in the MS gives *m*/*z* 109 (M^+ -CH_3), while further decomposition of this ion through CO elimination gives *m*/*z* 81 (M^+ -CH_3 -CO). A similar fragmentation pattern is observed for 4-vinylguaiacol and syringol. Most other peaks in this pyrogram correspond to methoxyphenolic compounds as well. In addition, a broad peak at 18–20 min (Figure 1.3a) derives from levoglusocan, which is the principal pyrolysis product of cellulose (including hemicellulose). These results show that, unsurprisingly, gorse wood consists almost completely of lignin and cellulose, i.e. lignocellulose. c) Corresponding molecular structures. d) The macromolecular representation of lignin illustrates from which moieties in the lignin macromolecule the detected peaks may originate. Red wave symbols in that figure represent sites where pyrolytic cleavage may have occurred, thereby producing the aforementioned methoxyphenolic pyrolysis products I–III. Interpretation of the pyrolysis-GC/MS fingerprint of fresh wood is relatively straight-forward: more complex samples consisting of admixtures of many biocomponents in various stages of decomposition, such as SOM, are far more complex.


a)
abundance [-]
retention time [min]
I
II
III
b)
m/z
c)
2-methoxyphenol
guaiacol
4-ethenyl-2-methoxyphenol
4-vinylguaiacol
2,6-imethoxyphenol
syringol
d)

Halfway the 1980s, pyrolysis-GC/MS began to be widely applied in molecular characterisation studies of SOM. Pyrolysis-GC/MS studies of SOM benefited greatly from the growing body of research on the pyrolytic behaviour of isolated and purified samples of the biocomponents discussed in Section 1.1.2 (cellulose and other carbohydrates: Browne, 1958; Pouwels et al., 1989; Boon et al., 1994; Sanders et al., 2003; chitin: Stankiewicz et al., 1998; Bierstedt et al., 1998; lipids: Tegelaar et al., 1995; Nierop and van Bergen, 2002; Boom et al., 2005; proteinaceous biomass: Tsuge and Matsubara, 1985; Chiavari and Galletti, 1992; Schulten and Schnitzer, 1998; tannins: Galletti et al., 1995; Ohara et al., 2003; lignin: Sáiz-Jiménez et al., 1987; del Río et al., 2002), and their microbial degradation products. The results from isolated biocomponents allowed for tentative source allocation of pyrolysis products from complex SOM mixtures and also track degradation mechanisms in the soil environment (e.g. Huang et al., 1998; Nierop and Buurman, 1999; Buurman et al., 2007a, 2007b).

On the other hand, several disadvantages of the pyrolysis technique became apparent: (1) pyrolysis not only produces volatiles that can be analysed but also a carbonaceous solid and a liquid product from the condensation of volatiles (tar). The relative proportion of volatiles and tarry and carbonaceous residues differs widely between different materials and pyrolysis conditions (e.g. polymethyl methacrylates are completely volatilised, keratin produces a major amount of tar while graphitic BC is largely non-pyrolysable). (2) Different materials pyrolyse to characteristic GC-amenable products at different temperatures (Marbot, 1997; Wampler, 1999), so that the ‘optimum’ pyrolysis temperature varies between them. A temperature that is too low will leave a large residue of non-pyrolysed matter. On the other hand, pyrolysis at excessively high temperature will produce extensive bond breaking but may also destroy characteristic chemical moieties and give an array of small and non-specific pyrolysis products. Thus, pyrolysis of polymers with thermolabile linkages, such the glucosidic bonds between the monomers of polysaccharides, may be optimal at temperatures between 400 ºC and 550 ºC, while thermally recalcitrant materials (e.g. coal, charcoal or soot) require more energy for macromolecular breakdown and therefore higher pyrolysis temperatures (Sáiz-Jiménez, 1994a). For complex mixtures, the analyst must compromise to a most appropriate pyrolysis temperature for the whole set of materials present, typically between 500 ºC and 800 ºC (Wampler, 1999). (3) During and immediately after pyrolysis, a series of structural rearrangements might occur, such as elimination of functional groups (e.g. decarboxylation), cyclisation of linear aliphatic C chains, degradation of N-containing functional groups and recombination of reactive intermediates (Chiavari and Galletti, 1992; Martín et al., 1994). These rearrangements destroy diagnostic groups of SOM components and produce structures that did not occur in the original sample, which significantly limits the structure-elucidating power of pyrolysis-GC/MS and urges for major caution in the interpretation of pyrograms (Sáiz-Jiménez,

1994a/b, 1995). (4) High-polarity compounds (e.g. polycarboxylic acids and polyhydroxylic aromatics) are poorly separated on the commonly used non-polar GC column when not pre-treated with a derivatisation agent and may therefore become barely discernible (Dignac et al., 2006). (5) Considering the multitude of pyrolysis products from natural polymers such as SOM, it is impossible to account for differences in MS response factors, which implies that the method can only be used as a semi-quantitative tool. Nonetheless, pyrolysis-GC/MS often provides a good estimate of the relative proportions of biocomponents, as suggested by the close agreement with the results of the quantitatively more reliable NMR techniques (Sáiz-Jiménez et al., 1987; Kaal et al., 2007). (6) The presence of mineral particles catalyses some pyrolysis reactions while inhibiting others, thereby further complicating the interpretation (Alcañiz et al., 1989; Schnitzer et al., 1994; Miltner and Zech, 1997; Nierop and van Bergen, 2002; Zegouagh et al., 2004). For these reasons pyrolysis products cannot be considered building blocks of the macromolecule analysed and knowledge of pyrolysis reactions is required for extracting useful and reliable information from pyrolysis-GC/MS analyses (Kögel-Knabner, 2000; 2002). In fact, pyrolysis-GC/MS has been referred to as a 'two-edged sword' because of the large amount of information it provides on the one hand while, on the other hand, severe errors may arise from the incorrect interpretation of this data (Janoš, 2003). Despite these limitations, pyrolysis-GC/MS has proven a valuable tool in the molecular characterisation of SOM and of polymers from diverse fields, e.g. forensic studies (car paint, documents, human hair), product analysis (cosmetics, cigarettes, tire rubber), art and archaeology (pottery, food residues, paints, varnishes, amber), petroleum geochemistry (coal, kerogen), etc.

1.2.3 Pyrolysis-GC/MS of Black Carbon

In addition to the aforementioned limitations of the pyrolysis-GC/MS technique (Section 1.2.2) for non-pyrogenic SOM constituents, pyrolysis-GC/MS of BC poses further obstacles. First, a relatively large proportion of the material is non-pyrolysable because of the relatively high thermal stability of burning residues, and therefore a larger fraction escapes the analytical window (González-Vila et al., 2001; Poirier et al., 2003; Rumpel et al., 2007). Second, structural reorganisation in the pyrolysis chamber mimics thermal impact during natural charring (Saiz-Jiménez, 1994a, 1995; Wampler, 1999). This implies that two thermal degradation mechanisms need to be distinguished. Finally, BC has, apart from polyaromatic moieties, no functional groups that produce marker compounds upon pyrolysis. For example benzene and toluene, which are typically the principal pyrolysis products of BC, are also produced from many other aromatic and non-aromatic precursors such as lignin, protein, carbohydrates and tannin.

Nonetheless, a substantial body of research aimed to probe the chemical properties of BC using pyrolysis-GC/MS, with limited success. They confirmed the obvious aromatic nature of BC (González-Pérez et al., 2004) and the enrichment of PAHs after charring (Naafs, 2004; Ross et al., 2005; de la Rosa Arranz, 2007; Rumpel et al., 2007; de la Rosa Arranz et al., 2008), and provided information on the susceptibility of different biocomponents to thermal impact (e.g. González-Vila et al., 2001; Schnitzer et al., 2007). Some of the analytical conditions and interpretation strategies that were commonly used, however, explain at least part of the sparse added knowledge on BC chemistry gained from this technique: (i) the majority of the studies applied a low pyrolysis temperature, which promotes incomplete pyrolysis (mostly at 500–510 ºC: González Vila et al., 2001; Knicker et al., 2005b; Rumpel et al., 2007), ii) they focussed on pyrolysis products of uncharred biomass and not on the products obtained from the BC itself, (iii) generally, the pyrolysates were not discussed in detail and important pyrolysis products such as benzene were frequently ignored, and (iv) the pyrograms were rarely quantified, rendering it difficult to compare studies and impossible to link BC properties to relative proportions (ratios) of pyrolysis products. However, the most fundamental problem is that there had been very few methodological attempts to optimise the pyrolysis conditions for BC and to create a framework for pyrolysate interpretation, with the notable exceptions of Boon et al. (1994) and other contributions from his group.

1.3 The study area

1.3.1 Geographical setting

The study area is the Rock Art Park of Campo Lameiro (42º32'N 8º31'W; U.T.M. coordinates: X: 538797; Y: 4710597), on the upper part of the Monte Paradela hill (260–320 m a.s.l.), near the Paredes parish in the municipality of Campo Lameiro (Pontevedra, Galicia, NW Spain), at a distance of 25 km east of the Atlantic Ocean (Figure 1.4). The Monte Paradela hill lies in a small basin surrounded by larger hills (> 600 m a.s.l.) that form part of the western margin of the Dorsal Gallega, a mountain range that separates the Atlantic region (Sector IV) from inland areas in NW Spain (see Martínez Cortizas et al., 2009). Conditioned by Atlantic cyclones, the climate is mild and humid, with an average annual temperature of 15 °C (9 °C in winter and 21 °C in summer) and an annual precipitation of 1200 mm. Rainfall is concentrated in the autumn and winter months (Martínez Cortizas and Pérez Alberti, 1999). The excessive rainfall drained through N-S and NE-SW directed faults deeply incised 'the Galician granite block', creating a hilly landscape mostly between 150 and 500 m above sea level. The dominant rock type of Monte Paradela is coarse granite of the Laxe group (IGME, 1982).

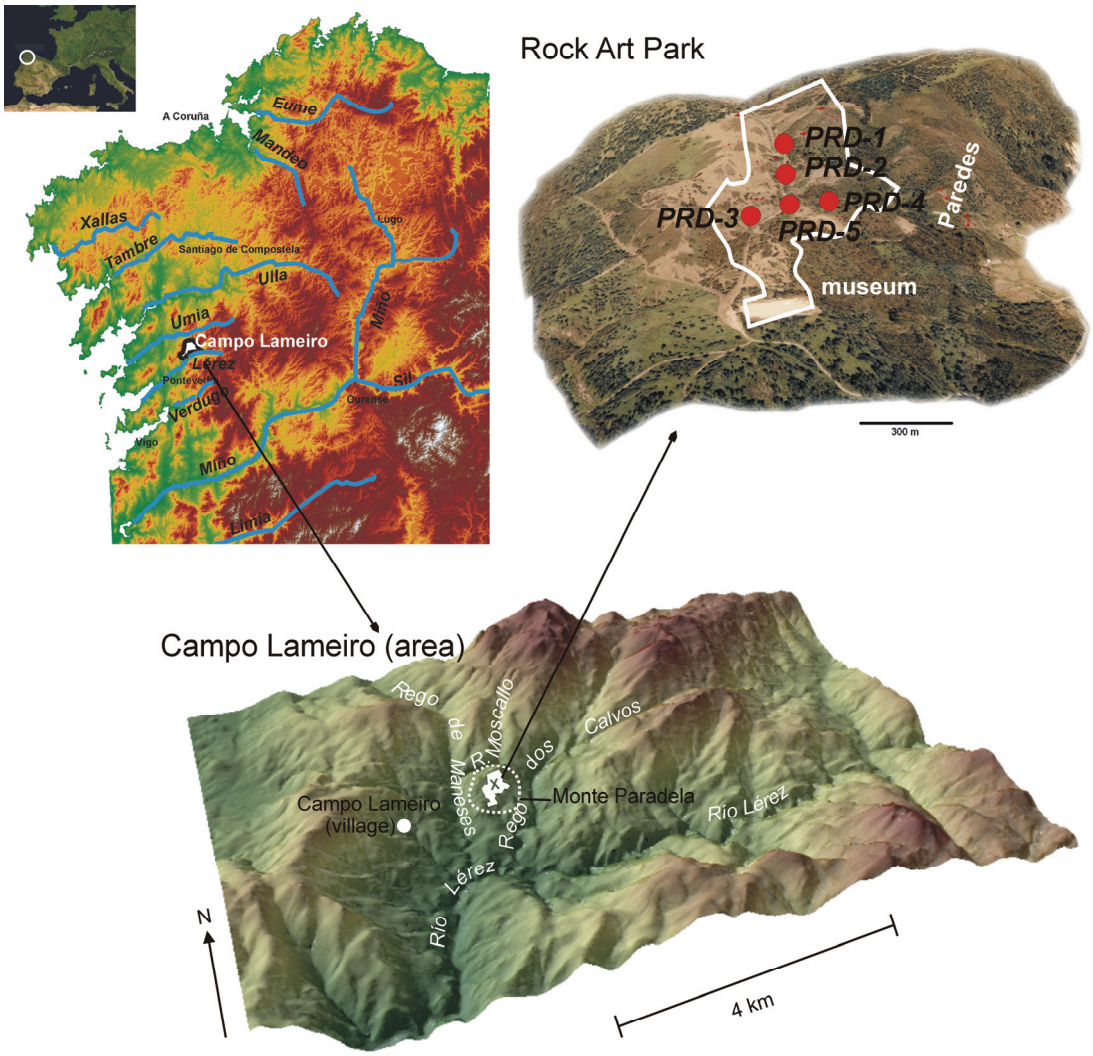


Figure 1.4: Location of the study area. Red dots mark the sites where soil columns were taken (Section 1.3.4).

1.3.2 Actual vegetation

The study area belongs to the Eurosiberian phytogeographic zone, where mixed deciduous forest dominated by pedunculate oak (*Quercus robur*) is the most abundant vegetation type in undisturbed areas. In the municipality of Campo Lameiro the deciduous forest is largely destroyed and the few remaining patches of oak woodland are highly fragmented, as in most of NW Spain. The riparian vegetation (e.g. alongside the Río Lérez and Rego de Maneses; Figure 1.4) is characterised by a combination of typical riverside tree communities consisting of alder (*Alnus glutinosa*), ash (*Fraxinus spp.*), hawthorn (*Crataegus monogyna*), elm (*Ulmus minor*), poplar (*Populus* spp.) and hazel (*Corylus avellana*), often in

association with *Q. robur* and birch (*Betula sp.*). At short distances to the river, the tree vegetation is dominated by *Q. robur*. Further upslope, a transition from *Q. robur* towards a complex mosaic of shrub communities, tree plantations and pasture grounds can be observed. The most abundant species in the shrublands are heathers (*Erica* spp.), gorse (*Ulex* spp.), broom (*Genista* spp., *Cytisus* spp.) and heather (*Calluna vulgaris*). This mosaic at the upper slopes and flats is locally known as *o monte*[4]. The shrublands are thought to be a product of anthropogenic deforestation and form a disclimax stage in vegetation succession. The disclimax vegetation is maintained by the limited forest regrowth which may be attributed to the intense disturbance regime (fire, grazing) imposed on *o monte* (Pesqueira et al., 2005). Reafforestation practices, mainly of pine (*Pinus pinaster*) and eucalyptus (*Eucalyptus globulus*), caused a shift in the vegetation. These plantations replaced shrub communities and pasture ground, especially in the course of the 20th century (van Mourik, 1986). Before this transition, the shrub communities were of major socio-economic importance (e.g. Bouhier, 1979; Balboa López, 1990). Ferns are abundant in virtually all of these communities. The pattern of riperian vegetation, dispersed oak woodland, shrubland, pasture and pine and eucalyptus plantations, illustrated here for Campo Lameiro, is typical of the undulating hilly landscape of NW Spain (Annex I).

The study area is on top of the Monte Paradela and forms part of the *o monte* landscape. The vegetation is dominated by the corresponding species mentioned above (heather, gorse, fern, etc.) (Annex II). However, in 2003 and again in 2009, eucalyptus and shrub communities were eliminated (Rey García et al., 2004), aiming to recreate an open oak-dominated woodland in the park area.

1.3.3 Archaeological setting

The municipalities of Campo Lameiro and Cotobade harbour an exceptional concentration of Galician (or Atlantic-style) open air petroglyphs. The rock carvings, most of which in granite, can be divided in two main classes: abstract geometrical figures (concentric circles, squares, spirals, labyrinths, etc.) and figurative representations of arms (e.g. daggers, swords, halberds and shields), zoomorphs (mainly horse and dear) and anthropomorphs. Depictions of weapons and warriors, which probably had a strong territorial as well as symbolic meaning (power, status, courage), are often found on oblique panels for better visibility, while dear depictions

[4] In Galician, the term *o monte* corresponds to areas of a specific type of extensive land-use management (pasture, slash-and-burn agriculture, gorse cultivation and wood production) in uphill areas of anthropisised landscapes. *O monte* does not refer to a 'hill' or 'mountain' in the sense of *monte* in the Spanish language (as in Monte Paradela, for example). See Bouhier (1979) and Balboa (1990) for details.

and the geometrical figures, which are more closely related to a poorly understood symbolic universe of past societies, are predominantly found on horizontal panels (Sobrino Buhigas, 1935; de la Peña Santos and Vázquez Varela, 1979; Santos Estévez, 2007). There is general agreement that the vast majority of the Galician rock carvings stems from the Bronze Age (Bradley and Fábragas Valcarce, 1998; Santos Estévez, 2005). Nonetheless, the chronology of the rock carvings is still under debate. Currently, two main proposals exist. The first argues that virtually all Galician rock art is from a brief period of time, viz. the Early Bronze Age (ca. 4500–3700 cal BP) (e.g. de la Peña Santos and Rey García, 1993), while others argue for a wider time frame that covers the the Late Neolithic, the Bronze Age and initial phases of the Iron Age (ca. 5000–2500 cal BP) (Santos Estévez, 2007). The approach of the wider time frame pays more attention to similarities with the carvings from other areas in Europe (e.g. United Kingdom, Scandinavia and Italy) and refers to the rock carvings as Atlantic-style rock art, while those that support the Early Bronze Age scenario (and subsequent social crisis in the Middle Bronze Age) often refer to the carvings as the Galician Group of rock art.

In general, the rock carvings are nowadays found in pasture, shrubland and reforestation areas (*o monte*). The vast majority of the petroglyphs in Campo Lameiro and Cotobade are located between 200 and 400 m a.s.l. (Parcero Oubiña et al., 1998; Santos Estévez and Seoane Veiga, *in press*), while higher-altitude flats and especially valleys are typically devoid of engravings. The location of the petroglyphs on the altitudinally middle parts of the slopes, which are easily accessible sites that offer great visibility over the landscape (if sufficiently deforested), reflects the intimate relationship between the territorial organisation of the landscape and petroglyphs patterns in space (Bradley et al., 1995; Santos Estévez and Criado Boado, 1998, 2000).

The first archeological excavations in the area of the Rock Art Park of Campo Lameiro were near and on top of the *Os Carballos* petroglyph (Annex II), located next to soil PRD-2 (Section 1.2.4). The excavated colluvium produced very little or no archaeological remains (de la Peña Santos, 1982, 1985). Later excavations from the park area and other sites with rock carvings would show that the paucity of archaeological remains, notably ceramics and lithic elements, is typical of the soils surrounding the petroglyphs. Between 2003 and 2004, more than two kilometers of trenches (Figure 1.5) were dug in the park area and soil columns were taken from these trenches, which are the main subject of this thesis. Many of the colluvial soils contain conspicuous soil layers with large stones, up to 20 cm. Whether these reflect intense erosion or were deposited by humans remains unknown. Again, archaeological remains were exceptionally scarce (Prieto Martínez, *in press*).

More recently, excavations near the actual site of the CIDAR did give ‘positive’ results. Excavations in 2005 brought to light a series of structures that seem to be the remains of the floor of ca. 3 m diameter huts (*fondos de cabaña*), pits and post holes,

yet again with no other cultural remains (Bonilla Rodríguez and César Vila, *in press*). Additional findings of prehistoric hut structures and post-holes were excavated in 2008 in the area that is nowadays the parking lot (Méndez Fernández and López Alonso, *in press*) (Annex II). Anthracological analyses of charcoal from these circular structures showed that *Q. robur*, woody legumes (Fabaceae) and strawberry tree (*Arbutus unedo*) were the main sources of the charcoal (Martín Seijo, *in press*). These results have yet to be placed into their archaeo-ecological and palaeo-environmental perspectives. In summary, there is a discrepancy between the apparently large number of the remains of structures that are suggestive of a significant settlement and, on the other hand, the lack of cultural remains that such populations would normally leave behind. The archaeologists in charge of the last excavation attributed the scarcity of other remains to strong erosion episodes after abandonment of the site (Méndez Fernández and López Alonso, *in press*). Alternatively, the lack of evidence of domestic activities may suggest that the area was not permanently settled but served for other means instead, such as occasional ritual activities, and only for a short period of time (Santos Estévez, 2007).

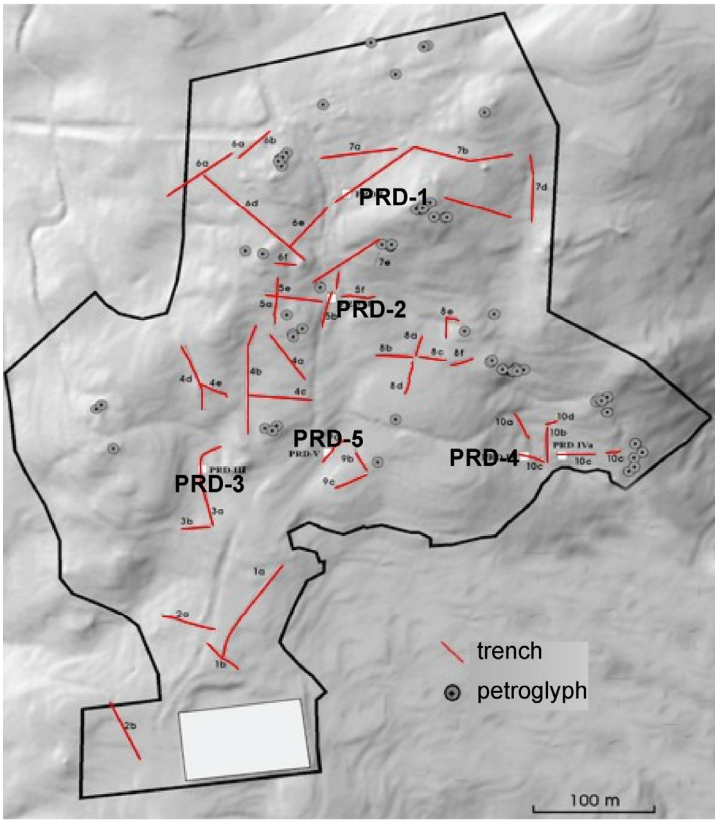


Figure 1.5. The Rock Art Park of Campo Lameiro (black polygon) with the trenches from activities in 2003 and 2004 (red lines), the main petroglyphs in the area (circles) and the site where the CIDAR is located (white rectangle). Figure elaborated by the GIS group of the *Laboratorio de Patrimonio* of the *Consejo Superior de Investigaciones Científicas* (LaPa-CSIC).

The Campo Lameiro municipality contains a series of fortified settlements belonging to the so-called Hillfort culture (*Cultura Castrexa*, the Iron Age of the NW Iberian Peninsula). The Celtic nature of this culture is discussed elsewhere (e.g. Armada Pita, 2002; González García, 2007; García Quintela and Santos Estévez, 2008). In the close proximities of the *Castro de Penalba*, located at less than two km from the CIDAR, at 420 m a.s.l., excavations and the study of charred caryopses provided evidence of crop production (wheat and millet) around ca. 2700 cal BP, which forms the most compelling evidence of prehistoric cereal agriculture in the area (Álvarez Núñez 1986, 1987; Aira Rodríguez et al., 1990). Pollen spectra from that period are dominated by herbaceous species, Ericaceae and Asteraceae, with lower proportions of tree species (*Quercus* sp., *Corylus* sp. and *Alnus* sp.). Furthermore, small contributions of chestnut, cerealia, plantain (*Plantago* sp.) and nettle (*Urtica* sp.) were observed, pointing towards a strongly anthropisised and deforested landscape (Aira Rodríguez and Saá Otero, 1998).

Due to the scarcity of archaeological remains other than rock art, the function of the area (ritual site, hunting ground, pastureland, small-scale agricultural practices, nutrient/fuel source, etc.) and its changes through time remain to be investigated. Previous analyses and radiocarbon dating showed that the vast majority of the constituents of the soils of the Rock Art Park of Campo Lameiro predate the Late Medieval Period so that the area offers an excellent opportunity to study Holocene landscape changes and human activities, and the complex feedback mechanisms between them, in an archaeological 'hotspot' area.

1.3.4 Soils of Campo Lameiro: Atlantic rankers

The incorporation of organic material into soil surface layers produces A-horizons. The continuous formation and redistribution of these A-horizons –mixed with weathered parent material with no organic component– through slope transport created shallow soils and rock outcrops at high potential energy sites (high slope angle, runoff erosion pathways, etc.) and thick soils at low potential energy sites were net accumulation occurs (local depressions, or alveoli). The shallow soils are mainly Haplic Leptosols (humic) and Umbric Leptosols (humic) in the WRB classification system (International Union of Soil Sciences, 2006). The thick soils in local depressions are Haplic Umbrisols (humic/alumic). Both soil types have AR or AC horizonation. The soils studied here are of the Umbrisol type, which are discussed in more detail below.

The soils studied are deep (> 1 m thick) organic matter-rich colluvial deposits that formed in the local depressions of the Monte Paradela hill. Alternating phases of landscape stability (limited erosion, development of A-horizons) and instability (continuous removal of SOM-rich surface material or superficial saprolite, usually

associated with a reduced vegetation cover) produced polycyclic soils consisting of buried endorganic horizons. The polycyclic nature of this type of soil is evidenced by the regular observation of stone-rich layers and other discontinuities, which reflect changes in the composition of the material transported by colluviation (Blaser et al., 1997; Bäumler, 2001; Bäumler et al., 2005). As a consequence of their polycyclic pedogenic origin, any designation of these soils is unsatisfactory (Mücher et al., 1972; van Mourik, 1999). They key out as Haplic Umbrisols (humic/alumic), but this soil type includes non-colluvial soils with a clearly distinct pedogenetic history of that of the colluvial soils studied here. Therefore, in this work, the soils of the study area are referred to as 'Atlantic rankers' (Franz, 1956), which more adequately reflects the idiosyncracies of these soils.

Apart from the formation through colluviation, Atlantic rankers are characterised by their high SOM content, low pH (3.5–5.5, in water) and the abundance of poorly-crystalline ('active') Fe and especially Al (oxy)(hydr)oxides. These properties are mutually dependent: the rapid binding between SOM and poorly-crystalline Fe and Al phases mitigates degradation of the former and crystallisation of the latter (Carballas et al., 1967). More specifically, the SOM is protected against biological decomposition –mainly by saprophytic bacteria and fungi (Acea and Carballas, 1990)– because its functional groups are masked from the microbial community by the covalently bound Fe and Al phases (Carballas, 1982, Macías et al., 1982), which reduces its mineralisation rate up to 4-fold (Schwesig et al., 2003; Schneider et al., 2010a). As a consequence, the complexes of poorly-crystalline mineral phases and SOM are very slowly decomposed and the soils obtain an acidic (low pH) and 'fluffy' (low bulk density) character, similar to non-allophanic (aluandic) Andosols (García-Rodeja et al., 1987, 2004). The replenishing of Al and Fe phases is controlled by the weathering of the parent material. As such, Atlantic rankers are often found in areas with acidic parent rock. Atlantic rankers are ubiquitous in NW Spain, which may be ascribed to the combination of high primary production, high humidity and the dominant granitic substrate that produces large amounts of poorly-crystalline Fe and Al (oxy)(hydr)oxides upon weathering. In NW Spain, Atlantic rankers are concentrated on the middle and upper sections of gently sloping hills, which corresponds largely to the *o monte* terrain. It was previously thought that the coincidence of Atlantic rankers with shrub-dominated vegetation at the upper part of gently sloping hilly landscapes, surrounded by areas with relatively intact forest vegetation, may be explained by the action of strong winds in the Atlantic bioclimatic zones, inhibiting the development of uphill forest vegetation (Duchaufour, 1982). Nowadays, this link is commonly attributed to soil erosion, soil degradation (high Al-saturation of the exchange complex, low pH) and, as aforementioned, land use strategies (Martínez Cortizas et al., 2009).

The depth profiles of SOM concentration and bound Fe and Al (oxy)(hydr)oxides in various Atlantic rankers were suggestive of significant

translocation of organo-mineral complexes (podzolisation), invisible to the eye as a result of the dark colour throughout the soil. Therefore, these soils have been referred to as cryptopodzolic soils (Carballas et al., 1967; Duchaufour, 1982; Blaser et al., 1997; Eckmeier et al., 2010). The large amount of poorly-crystalline Fe and Al (oxy)(hydr)oxides that is released upon weathering, however, causes the precipitation of Al-saturated organic matter close to its source (Carballas et al., 1967; Aran et al., 2001), and some rankers were therefore referred to as 'abortive podzols' (Delvaux et al., 2004). Duchaufour (1982) described intermediate soils called 'andic rankers'. Other humiferous soils with abundant poorly-crystalline Al phases and SOM were called umbric soil, aluminic soil, humiferous Atlantic soil or acid humic ranker (Carballas et al., 1978a; Macías et al., 1982; Condron et al., 1993; Álvarez et al., 2002; Camps Arbestain et al., 2003). All these denominations refer to thick colluvial soils with high SOM and poorly-crystalline Fe and Al (oxy)(hydr)oxides contents.

The SOM of Atlantic rankers from NW Spain is particularly 'difficult' to examine and has been the source of debate for decades (see e.g. Macías Vázquez, 2003). Organic matter characterisation studies focussed on the isolation and analysis of the elemental composition and sometimes functional group properties of traditional SOM fractions (after chemical extractions). It became clear that the SOM in Atlantic rankers is characterised by a high degree of humification, that the SOM is dominated by humic acids (approximately 80 %) and that it is highly resistant to microbial attack (Rodríguez Seoane et al., 1975; Carballas et al., 1978b) and to laboratory hydrolysis (Carballas et al., 1978a). The humic acids are rich in N and highly aromatic in nature (Carballas et al., 1978a), with abundant phenolic and carboxylic functionalities (Rodríguez Seoane et al., 1976). Charcoal fragments are frequently observed (Franz, 1967; Texier et al., 1989; Bertran et al., 1991; Martínez Cortizas et al., 2000). Nonetheless, the slow decomposition of the SOM is, as aforementioned, traditionally attributed to the protective effects of abundant poorly-crystalline Fe- and Al-hydroxides and, in an auxiliary manner, the intrinsic aromatic and polymeric nature of the SOM. According to Duchaufour (1982), the polymeric nature of the SOM may be related to the effects of warm and dry summer periods stimulating polymerisation reactions of the humic acids. The C/N ratio of the buried horizons of Atlantic rankers is typically between 10 and 15. The N component of the SOM is remarkably resistant against acid hydrolysis and its mineralisation in the soil is very slow, giving rise to N limitation for plant growth, in spite of the high organic matter content. It was suggested that the current abundance of *U. europaeus* on these soils may be partially explained by its capacity to fixate atmospheric N in its nodules (González-Prieto and Carballas, 1978). The molecular properties of the SOM in Atlantic rankers have not been studied yet.

The soils of the Rock Art Park of Campo Lameiro, in the Paredes (PRD) parish, contain up to 14 % organic C (by weight), have a bulk density typically below 800

kg/m^3 and contain large amounts of organically bound Al (up to 20 mg/g soil) and Fe (up to 10 mg/g soil) (Kaal et al., 2008). These properties are typical for the black-coloured colluvial Haplic Umbrisols (humic/alumic) of NW Spain, which stand model for the Atlantic rankers of Western Europe (Duchaufour, 1982). All soils show discontinuities (gravel-enriched layers, stone lines, charcoal-enriched layers and burnt soil) in the depth profile (Figure 1.6). As aforementioned, these soils are sometimes referred to as 'cryptopodzolic' because of the apparent translocation of Al/Fe-organic matter complexes into subsurface horizons, but these layers are actually buried A-horizons with very limited or no mobility of the organomineral complexes (Delvaux et al., 2004; Kaal et al., 2008). The soils should therefore not be considered podzolic. Given the limited mobility of the SOM, the soils can be used as archives of environmental change by tracking changes in SOM composition in the depth sequence, analogous to other colluvial soils that accumulated in the Holocene (Kalis et al., 2003; Leopold and Völkell, 2007). Because the soils are located on the upper part of a hill, external sources are subordinate to the material formed on the hill itself, rendering the site ideal for local-scale palaeo-environmental and archaeological reconstructions.

These soils offer a good opportunity for palaeo-environmental reconstructions in an archaeological context by studying the molecular properties of the SOM because:

i. In 2005 (the start of the present project), studies on the soils were in an advanced stage: high-resolution sampling from five soil columns and subsequent sample treatment, analysis of bulk physicochemical parameters had already been performed.
ii. Radiocarbon datings from soils PRD-1 and PRD-2 suggested the soils cover at least the last 8500 years, which presumably represents the entire period of significant human impact to the landscape, including the period(s) of rock art creation.
iii. The soils are rich in organic matter.
iv. The study area is on an isolated hill, which implies that the bulk of the material of which the soils consist formed on the hill itself, enabling the assessment of the local human footprint.
v. The area is of special interest because of the concentration of prehistoric petroglyphs and the creation of the CIDAR.

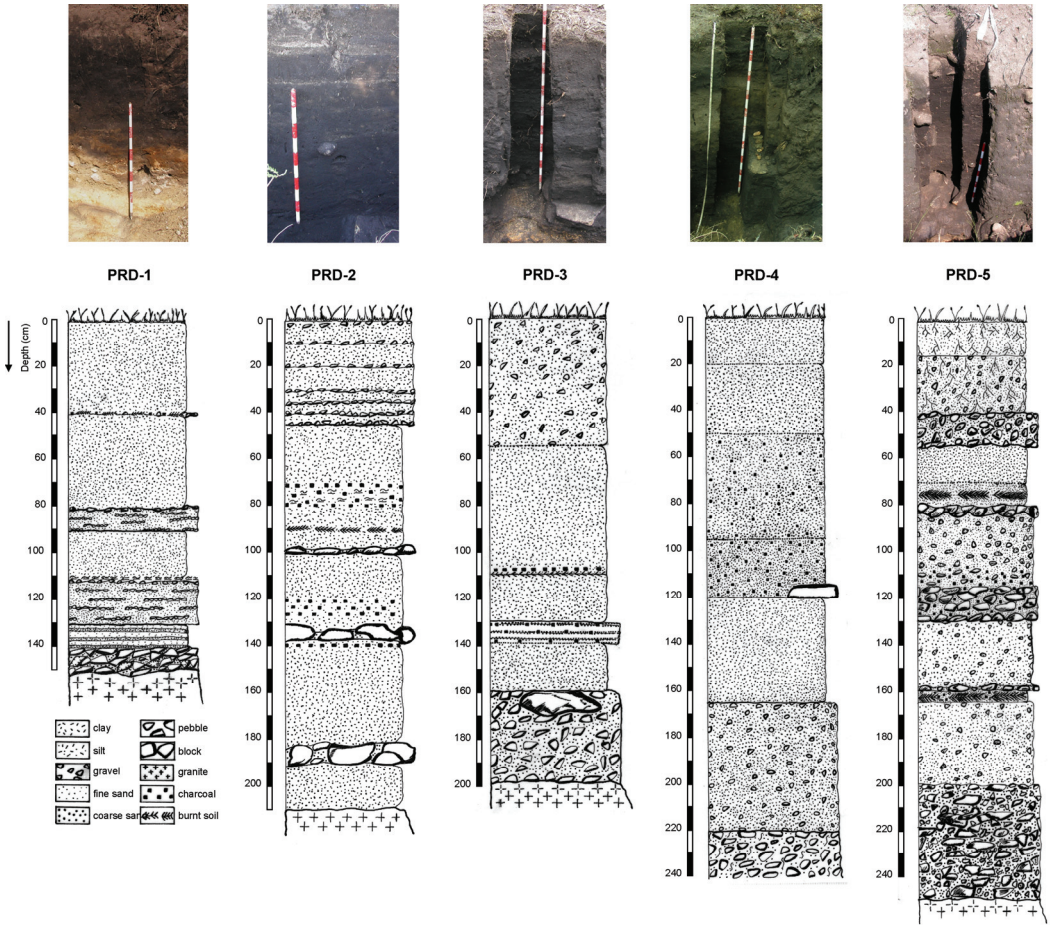


Figure 1.6: Photographs (C. Ferro Vázquez) and profile representations (M. Costa Casais) of the soils studied.

1.4. Scope and outline of this thesis

The objective of the research presented here was to gain information on landscape evolution and human activities in the Rock Art Park of Campo Lameiro by the application of molecular characterisation techniques on the SOM obtained from the colluvial soils that surround the petroglyphs. At the start of the project, the potential of SOM characterisation for achieving this main goal was unknown, because there had not been any previous palaeo-environmental or archaeological studies that used molecular fingerprinting of SOM from mineral soils in NW Spain, and the nature of SOM in Atlantic rankers was particularly enigmatical.

After it became apparent that the soils contained unexpectedly large amounts of fire residues, in combination with a lack of markers of specific human activities, it was decided to narrow down the scope of the research to the fire history of the area. Focus on fire history implied that tools other than molecular characterisation

techniques were required to (1) prove the abundance of finely-divided BC in the soils and (2) allow for a detailed reconstruction of the relation between fire, vegetation and human activities in the area. The main subjects addressed by this thesis are:

1. SOM dynamics in Atlantic rankers
2. Black Carbon: Molecular properties
3. Campo Lameiro: Fire regime, deforestation and human activities

Chapter 2 (Synopsis) of Part A of this thesis consists of a synoptic view of the three main subjects (Sections 2.1–2.3), a conclusions shortlist (Section 2.4) and recommendations for future research (Section 2.5). The bibliographical references of Part A are listed at the end of Chapter 2. The Synopsis (Chapter 2) aims to reconcile and elaborate further on the ideas presented in the papers published in peer-reviewed journals (Part B of this thesis). As such, Part B, which forms the main body of this thesis, may be considered as the scientific basis of the Synopsis.

CHAPTER 2: SYNOPSIS

2. SYNOPSIS

2.1 SOM dynamics in Atlantic rankers

It appeared that the Atlantic rankers from the Rock Art Park of of Campo Lameiro contained large amounts of BC from fire residues, probably as much as 30–40 % (by weight) of the SOM. A rough and conservative estimate of BC content – assuming an average soil thickness of 0.5 m, organic C content of 50 mg/g, bulk density of 800 kg/m^3 and BC content of 25 % of the C– gives 50 tonnes of BC per hectare (5 x 10^4 kg/ha). The amount of BC in the fine earth fraction is approximately 20 times as large as the amount present as macroscopic (> 2 mm) charcoal.

Black-coloured colluvial soils are widespread in the *o monte* areas of the low- and mid-altitude hills in Galicia (NW Spain), at 150–500 m a.s.l., presently covered for the most part by fire-adapted shrub communities or pine and eucalyptus plantations, but also in N Portugal and the autonomous communities Asturias and Cantabria in N Spain (Annex I). If future studies demonstrate that BC-rich Atlantic rankers are indeed widespread in these regions, they would form a huge reservoir of aged BC. In that case, the Atlantic rankers of NW Spain should be added to the list of soil types with large amounts of BC stored in it, including the *Terra Preta do Indio* soils (Amazonian Dark Earths) of Brazil (Glaser et al., 2001), cryptopodzolic soils surrounding the French Alps (Tinner et al., 2005; Hajdas et al., 2007; Eckmeier et al., 2010), Chernozems in Central Europe (Schmidt et al., 1999; Eckmeier et al., 2007) and Western Russia (Rodionov et al., 2006), various soil types from Australia (Skjemstad et al., 1996) and Japanese volcanic ash soils (Shindo et al., 2004).

From molecular characterisation, the SOM can be subdivided in the following types: (1) root-derived SOM, (2) primary SOM, (3) secondary/degraded SOM and (4) BC (Figure 2.1). The source of these types, their chemical characteristics and the degradation/preservation mechanisms operating on them are described below:

1. Root-derived SOM: Of the lipids, which account for ca. 10–30 % of the SOM, THM-GC/MS suggested that a significant fraction originated from roots. These root-derived lipids are probably incorporated into micro-aggregates, because no alternative structures except for occasional degraded root fragments were observed in thin sections, especially in the deeper layers of the soils. These lipids are protected to some extent because of chemical recalcitrance and probably also physical occlusion in micro-aggregates, while sorptive preservation through binding of poorly-crystalline Fe and Al phases is of less importance because of their small affinity towards mineral surfaces.

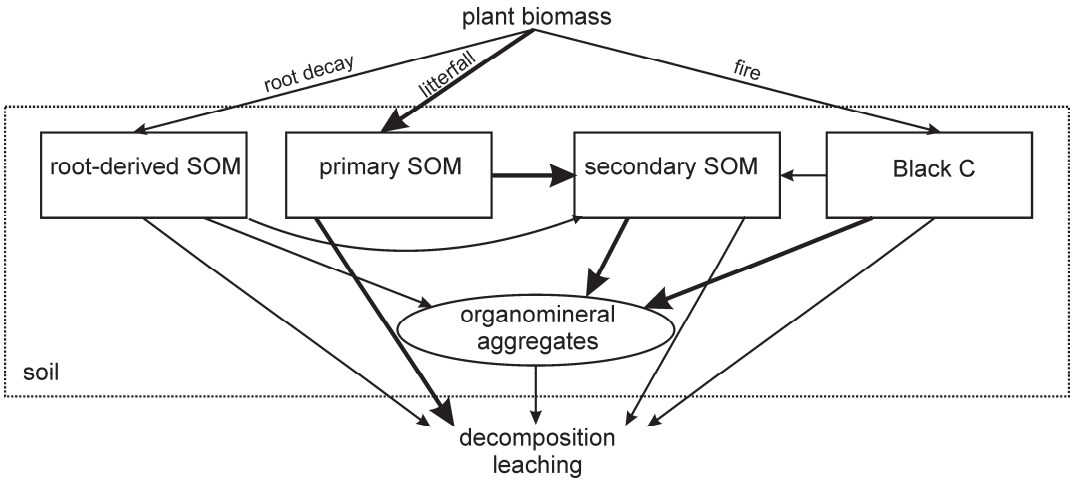


Figure 2.1: Schematic summary of SOM dynamics in Atlantic rankers.

2. Primary SOM: In the soils studied, primary SOM is an admixture of relatively intact polysaccharides, lignin, proteinaceous biomass and possibly a small proportion of the linear aliphatic substances (lipids, recognised in pyrolysates as fatty acids). Primary SOM is confined to the surface layers (0–15 cm depth) of the soils, in which the total contribution is always below 5 % of the extractable SOM. Thus, primary SOM is not protected against degradation and is not a significant SOM pool. These results suggest that the microbial degradation of primary SOM is sufficiently fast to inhibit its incorporation and protection in the soil's microgranular aggregates.

3. Secondary/degraded SOM: Secondary or degraded SOM accounts for approximately 30–50 % of the SOM. It forms a chemically diverse pool of substances including carbohydrate-, protein- and probably (non-root) lipid- and lignin-derived SOM, recognised in pyrolysates as furans, pyrroles/pyridines, *n*-alkanes/*n*-alkenes and phenols, respectively. An unknown proportion of this SOM may have been subjected to low impact thermal modification, i.e. it may partly consist of weakly charred biomass. Nonetheless, the secondary/degraded SOM should not be considered chemically recalcitrant. It is concentrated in the micro-aggregates of the microgranular soil matrix, in which it is probably stabilised against further microbial degradation by adsorption of poorly-crystalline Fe and Al phases as well as physical occlusion. In this sense, the soils studied show some resemblance to non-allophanic andic soils from NW Spain, in which secondary/degraded biomass accumulates in the micro-aggregates of buried horizons, where they are stabilised by Al binding and occlusion (Verde et al., 2008). The main difference with these soils is that the Atlantic rankers studied here contain large amounts of BC from palaeofires. The presence of fungal sclerotia (Annex III) in some thin sections might suggest that part of the secondary/degraded SOM originates from fungi. Nonetheless, neither

hyphae nor chitin were identified in thin sections and pyrolysates, respectively, suggesting that if fungal assimilation was a key process in SOM degradation, the fungal biomass is strongly degraded, except perhaps for some protected material in the sclerotia (below the detection limit of pyrolysis-GC/MS of the NaOH-extractable SOM).

4. Black C: BC appeared to be a major component of the SOM of the soils studied (ca. 30–40 %). Black C is relatively resistant against biological degradation because of its intrinsic recalcitrant nature. Nevertheless, the longevity of BC cannot be solely attributed to chemical recalcitrance, as shown by multiple recent studies that demonstrate BC decomposition on the decadal to centennial time-scale. Different morphologies of BC need to be distinguished in order to explain its preservation in the soils. Firstly, discrete SEM visible BC (Annex IV), including macroscopic charcoal and microscopic charcoal not incorporated into micro-aggregates, is very slowly decomposed primarily because of its chemical recalcitrance. Nonetheless, sorptive preservation may play a minor role here as well, as mineral particles were found to be adsorbed to aged charcoal (Annex IV). The SOM in the inner core of charcoal fragments that sometimes remains uncharred (Annex IV) was not detected in deeper layers of the soil, which implies that the inner part of charcoal fragments is sufficiently accessible to the microbial community to inhibit physical protection of uncharred biomass and BC in its own macrostructure. Secondly, finely-divided partially oxidised, depolymerised and depolyaromatised[5] aged BC is a major component of the organomineral micro-aggregates, which may thus be, in addition to the recalcitrance inherent to BC, stabilised by physical occlusion and enhanced sorptive preservation. It is very likely that the abundance of BC contributes significantly to the deep-black colour of these soils.

In conclusion, the Atlantic rankers store large amounts of SOM not only because of sorptive preservation by poorly-crystalline Al phases but also because of thermal stabilisation through fire and probably physical occlusion in micro-aggregates. In order to determine the relative importance of these three mechanisms, molecular-scale knowledge on SOM dynamics within the micro-aggregates would be required, which is not available for Atlantic rankers or similar soil types. With regard to the biological aspects of SOM dynamics in Atlantic rankers, van Mourik (1986) stressed the importance of earthworm activity in soil formation. However, tubular pores and

[5] Besides depolymerisation, ageing of BC during storage in soil involves aromatic ring opening processes that do not necessarily produce a decline in the size of the BC macromolecule. Nonetheless, because of simultaneous and often preferential degradation of non-aromatic groups, ageing of BC does not produce a relative decrease in aromaticity ("dearomatisation"), but rather a decrease in the size of polycyclic aromatic ring clusters. Tus, depolyaromatisation causes a decrease in the degree of polycondensation of the BC. Therefore, the term "depolyaromatisation" is preferred here. An analogous degradation process was referred to as "polyaromatic ring opening" by Rotaru (2009).

earthworm casts were not observed in the thin sections, and the few glaebules observed, which might originate from earthworm activity, were scarce. Therefore, the present studies do not confirm the importance of macrofauna activity in soil formation. Finally, no indications of cryptopodzolisation were found, which is subordinate to other SOM-related pedogenetic processes or may not occur at all.

If future research points out that Atlantic rankers indeed owe their SOM accumulation capacity largely to human-induced palaeofires, one could argue that they should be considered as Anthrosols, similar to the Brazilian Amazonian Dark Earths (International Union of Soil Sciences, 2006).

2.2 Black Carbon: Molecular properties

Combined results of the pyrolysis studies performed on BC allowed us to identify the changes in chemical properties with increased thermal impact, as seen by pyrolysis-GC/MS, for the major biocomponents sources of SOM (Figure 2.2). Briefly, with increasing degree of thermal impact the major effects of the lignin signature are C_3-side chain elimination (which promotes depolymerisation), demethoxylation, dehydroxylation and finally polycondensation. For carbohydrates even low-impact charring causes a strong decline in the proportion of levoglucosan from intact polysaccharides and an increase in furans. Further charring causes a shift from furans to benzenes and PAHs. With increasing degree of thermal impact the pyrolysis fingerprint of proteinaceous biomass shifts from pyrroles to pyridines to benzonitriles and polyaromatic nitriles. The straight-chain *n*-alkane/*n*-alkene pairs from uncharred lipids show progressive reduction in odd-over-even C number preference, chain-length shortening and eventually aromatisation. Additional pyrolysis studies suggested that the degree of dealkylation of pyrolysis products, which might reflect the abundance of short-chain aliphatic cross-linkages between aromatic moieties, can be a measure of thermal impact (Kaal and Rumpel, 2009; Kaal et al., 2010). This information will allow future studies to identify and characterise BC from pyrolysates and make a rough estimation of the proportion of BC and potentially its degree of thermal alteration as well. Recently, alternative methods that may allow for determining the degree of thermal impact are emerging (e.g. McBeath and Smernik, 2009; Schneider et al., 2010b). Pyrolysis-GC/MS should be tested against these methods to check for complementarity and consistency.

In comparison with recent charcoal, aged charcoal fragments provide pyrograms of high quality (strong total ion current, high signal-to-noise ratio), yet the pyrolysis signature of aged BC reflects relatively strong thermal impact. This suggests that heavily charred BC becomes progressively susceptible to pyrolysis during ageing in

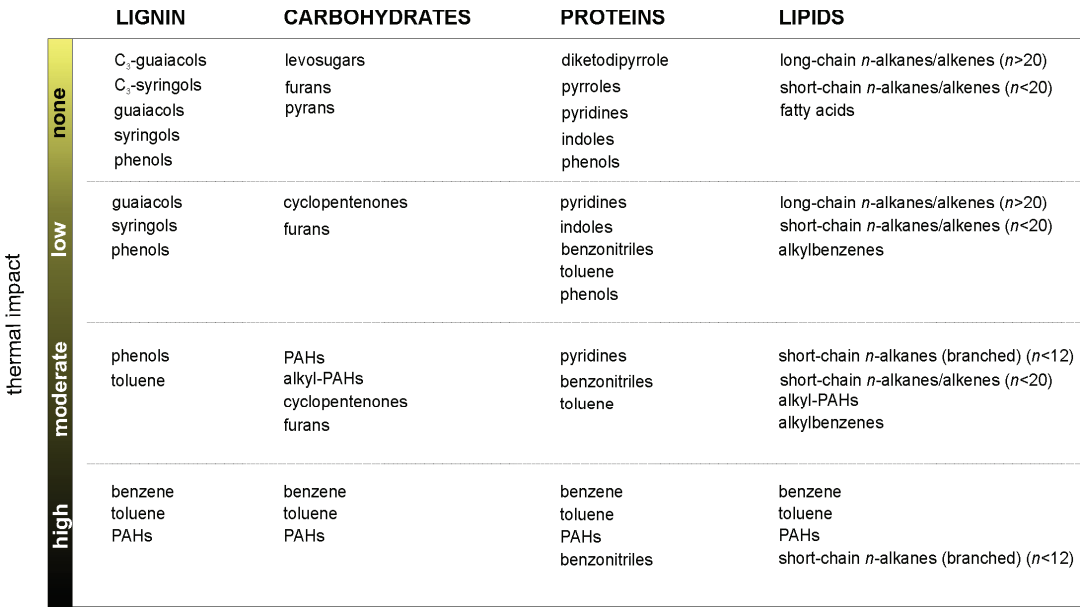


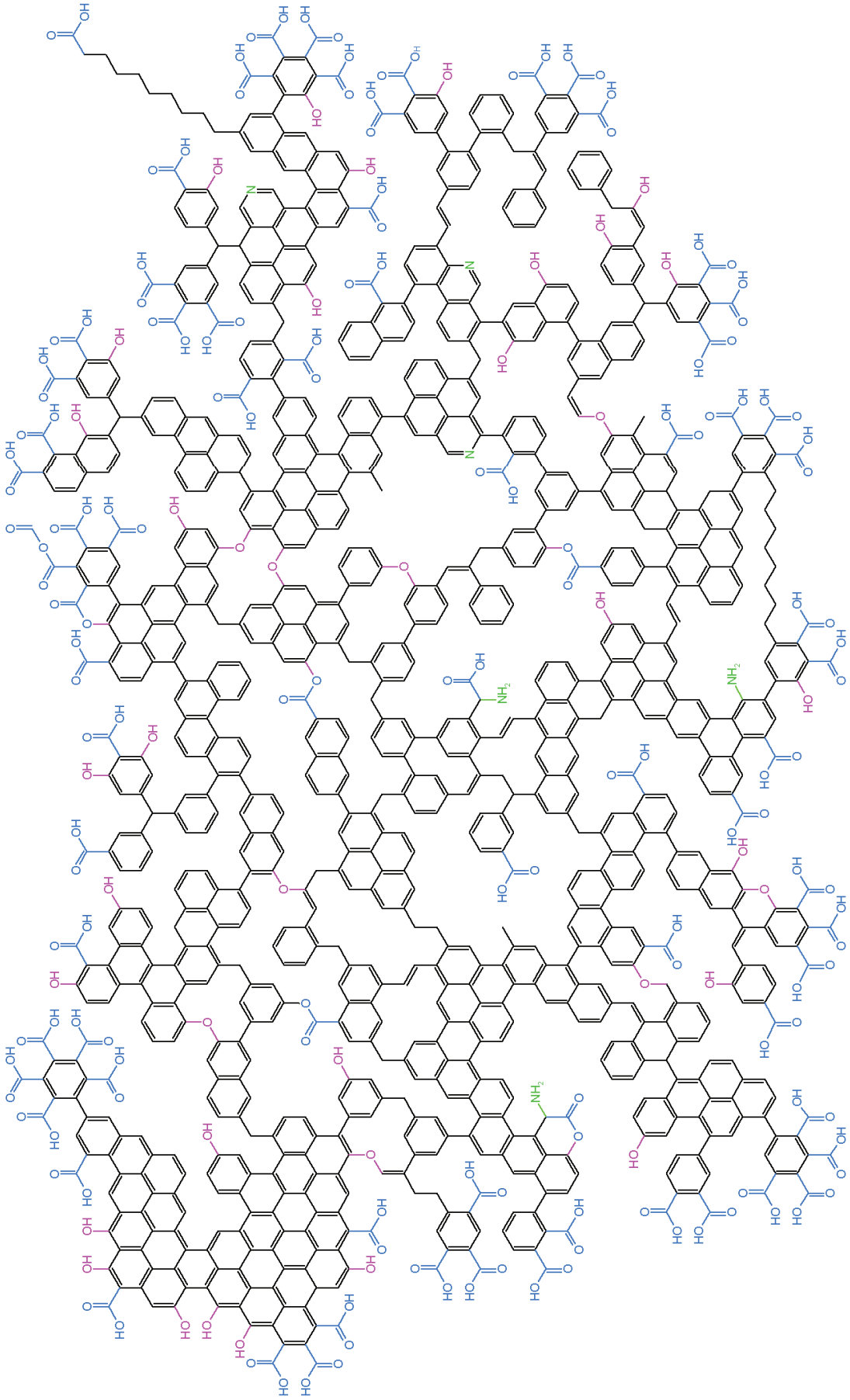
Figure 2.2: Changes in most abundant pyrolysis products of the main biocomponents upon increasing levels of thermal impact.

the soil environment. Pyrolysis at 750 ºC or lower may be safely expected to provide insufficient energy for breaking most of the C–C bonds in aromatics rings. Consequently, a large proportion of strongly condensed BC will give rise to a larger non-pyrolysable fraction. Henceforth, the enhanced signal for aged BC may be explained by depolymerisation/depolyaromatisation of BC during storage in soil. Depolymerisation and depolyaromatisation are initially caused by abiotic carboxylation of fresh surfaces (Cheng et al., 2006; Bruun et al., 2008), but the abiotic oxidation stimulates the microbial colonisability of the BC and with time the microbial community may induce significant degradation of BC. Oxidation, depolymerisation and depolyaromatisation of aged BC were confirmed by the high proportions of aromatic and carbonyl C in the DP NMR spectra, low yield of B4CA–B6CA in the BPCA method and the presence of methylated benzene polycarboxylic acids in the THM-GC/MS thermochemolysates.

Another effect of ageing is the loss of non-charred or weakly charred BC that frequently resides in the core of a BC particle from an incompletely charred plant fragment. The selective decay of non-pyrogenic and slightly charred biomass from BC specimens suggests colonisation by the decomposer community. Indeed, analysis of thin sections and charcoal fragments showed that many charcoal fragments were highly degraded and sometimes fungal hyphae or xylophague casts could be recognised in charcoal macropores. This supports recent evidence of biological activity on BC substrates (Carrión and Badal, 2004; Brodowski et al., 2005b; Warnock et al., 2007; Thies and Rillig, 2009; Moskal-del Hoyo et al., 2010).

To give a rough impression of what aged BC might look like at the molecular scale, a tentative 2D macromolecular model of aged wood-derived charcoal-BC was compiled based on the evidence presented in this thesis. For that purpose, we used data from four aged charcoal fragments (Manuscript 6) from soil PRD-1 (age ca. 3000–7000 yrs). The model is presented in Figure 2.3. The data used were obtained by elemental analysis (N/C ratio), pyrolysis-GC/MS (abundance of methylene chains), THM-GC/MS (abundance of (poly)carboxylated benzenes), DP NMR (proportions of aromatic, *O*-aromatic, *O*-alkyl, carbonyl and alkyl C) and the BPCA method (proportion of polycondensed moieties). It also takes results from other chemical characterisation studies of BC into account, such as the concentration of oxidised moieties on the external surfaces of a BC particle (Lehmann et al., 2005; Nguyen et al., 2009). The model, consisting of one thousand C atoms, would generally comply with the results of these methods. The model sketches a weakly condensed network of carboxylated aromatic building blocks linked through mostly C–C bridges, which is in rough agreement with the conceptual model described by Knicker (2007) and Knicker et al. (2008). Even though a 2D model is always a simplification of the macromolecular arrangement of chemical moieties in 3D, especially with small molecular moieties as the main building blocks of the molecular backbone, it is at least a significant improvement to the models available so far (e.g. Figure 1.1). One major difference between the descriptive model suggested by Knicker and co-workers for BC from recent vegetation fires and the model presented here for aged charcoal is that the aged charcoal is devoid of non-charred lignin moieties that may ‘survive’ charring (i.e., the methoxyphenolic structures remain intact), because such intact biomass is relatively easily decomposed during storage in soil and because some of these recognisable lignins may reside in an uncharred core that should not be considered as BC in the first place.

Figure 2.3 (next page): New macromolecular model of aged wood-derived BC, based on the results presented in this thesis. The model consists of one thousand C atoms.



Aged BC from non-woody plant parts (e.g. leaves and grasses) would have a higher N content, contain more heterocyclic aromatic groups (N, O and possibly S as well), have more short-chain alkyl cross-linkages and longer-chain (up to C_{20}) methylene-based aliphatics (Knicker et al., 2005b) than aged wood-derived charcoal-BC. This BC would be even more susceptible to microbial attack because it would be a more fertile substrate, less hydrophobic, more accessible structurally (more finely divided) and, on average, less (poly)condensed (Nocentini et al., 2010). It is impossible to postulate a macromolecular model of aged BC of these characteristics at this moment, even if differences in parent material and burning conditions would be ignored, for several reasons: 1) the arrangement of heterocyclic aromatics that form upon thermal alteration of peptides and polysaccharides (furans, pyrroles, pyridines) remains largely unknown, 2) whether and how longer-chain (C_{10}–C_{20}) methylene chains are incorporated into the aromatic network is unknown, 3) the signal of weakly-to-moderately charred biomass cannot be reliable separated from non-charred biodegraded organic matter in SOM admixtures (see also Knicker et al., 2008), and 4) the heterogeneity of the building blocks, with its inherent enhanced macromolecular complexity, causes increased doubt on the nature of the linkages.

The ideas presented here on the prevalence of small aromatic clusters in natural fire-derived BC and oxidised, depolymerised and depolyaromatised BC in aged mineral soil layers would explain why BC is often not as recalcitrant against degradation processes as previously thought: with time, an increasing proportion of the C atoms that constitute the BC would become subjected to abiotic surface oxidation (Cheng et al., 2008), reducing the hydrophobicity of the BC and opening the macromolecular arrangement, which allows the microbial community to colonise the newly-formed hydrated surfaces more efficiently than they would on the small proportion of C atoms at the external edges of polycondensed graphitic-like BC types. Strong oxidation of BC surfaces would also explain why it may become dissolved in soil solution (Hockaday et al., 2006), exported to riverine and oceanic C pools (Masiello and Druffel, 1998) and become incorporated into ‘highly aromatic humic acids’ (Kumada, 1983; Haumaier and Zech, 1995). In fact, partial oxidation, dissolution and fluvial transport of SOM from BC-rich Atlantic rankers may explain the abundance of BC in the pore water of marine sediments in the Miño shelf (Schmidt et al., 2009). The export of BC-derived organic matter to the oceans is of major interest for understanding the global cycling of BC and C in general. It is difficult to accept that any polycondensed soot-like or graphitic BC would undergo such extensive oxidation processes on time scales of years to decades. Novel insights in the properties of BC that evolved in oxic terrestrial soil is urgently needed in the context of biochar implementation in agricultural soils that aims to improve primary production, limit the loss of topsoil and sequester C from the atmosphere into relatively slow-cycling C pools.

2.3 Campo Lameiro: Fire regime, deforestation and human activities

Deciduous forest species dominated by oak (*Quercus robur*) started to replace a steppe-like association (mostly herbaceous species, *Betula* sp. and Fabaceae) around 10,000 cal BP. This forest prevailed between 8500 and 6000 cal BP, under the warm and generally wet conditions of the Holocene Thermal Maximum. Since then, the forest was progressively replaced by shrub communities –mainly of the genera *Erica* (heather), *Ulex* (gorse), *Cytisus and Genista* (broom)– and pasture ground. Meanwhile, exposure of the soil to wind and runoff erosion –following reduced vegetation cover– exposed granitic rock on the upper parts and the accumulation of soil material in local depressions (alveoli) in the area (Costa Casais et al., 2009). Remaining patches of forest became smaller and smaller, more dispersed and more fragmented. Figure 2.4 is a tentative representation of the landscape during the Holocene Thermal Maximum (deciduous forest optimum) and the eroded and deforested landscape since ca. 2000 cal BP.

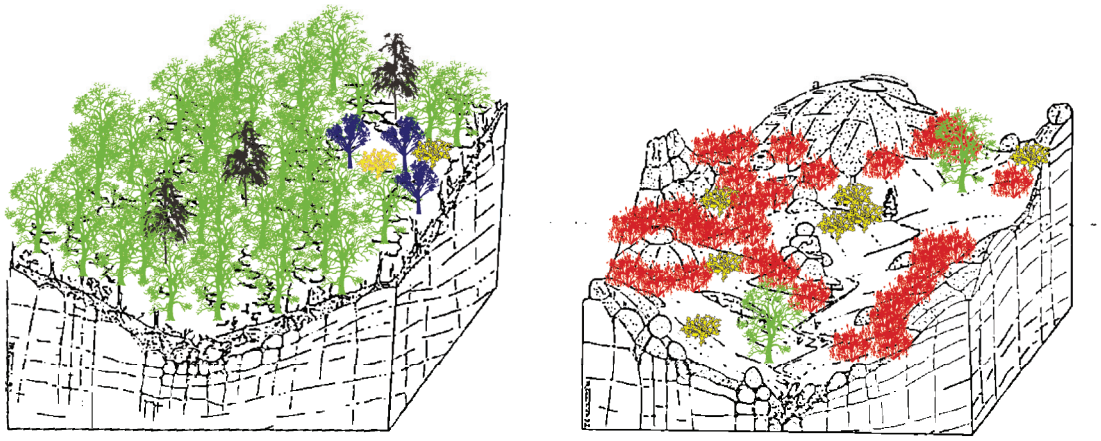


Figure 2.4: Illustrations of the landscape in the study area before (left) and after (right) elimination of the forest and subsequent erosion and rock exposure. The background landscape was modified after Pérez Alberti (1993). Legend: green = oak (*Quercus*), red = heath (*Erica*), yellow = shrub Fabaceae (*Ulex*, *Genista*, etc.), black = birch (*Betula*), blue = strawberry tree (*Arbutus*).

The stepwise destruction of the deciduous forest during the second half of the Holocene was most likely caused or stimulated by fire. The coincidence of accelerated deforestation and peaks in macroscopic charcoal content, in combination with the large concentrations of charcoal and finely-divided NaOH-extractable BC in virtually all layers of the soils studied, strongly suggests that fire was a major agent in the elimination of forest and shrubland expansion. Furthermore, most species detected are well-adapted to an intense disturbance regime, including fire. More specifically, the most likely candidates of the taxa tentatively identified from the

charcoal records (*Q. robur*, *Erica arborea*, *Betula* sp., *Arbutus unedo*, *Ulex* sp., *Cytisus* sp., *Genista* sp.) are resprouters (Mesléard and Lepart, 1991; Paula and Pausas, 2008; Reyes et al., 2009). Resprouting is an efficient post-disturbance strategy as long as the disturbance did not destroy the reproducing bodies, such as the upper root system (*Ulex* spp.), the lignotuber (*E. arborea*, *A. unedo*) or the epicormic buds on stems and branches (*Q. robur*). In addition, the germination of the seeds of the aforementioned Fabaceae is stimulated by the effects of fire (charcoal, ash, smoke and heat) (Reyes and Casal, 2008), while that of *Betula* sp., some Fabaceae and *E. arborea* is stimulated by light and thus by a reduction in tree cover (e.g. Rigueiro Rodríguez, 2002; Valbuena and Vera, 2002). Although *Q. robur* is able to resprout, it requires 25-30 years to reach sexual maturity and therefore a disturbance regime with intervals shorter than that will eventually lead to its disappearance through the exhaustion of its seedbank (cf. Sparrow and Bellingham, 2001). Thus, a high fire frequency can explain the substitution of *Q. robur* forest by the shrub communities observed. During climatically benign periods, a high fire frequency in the study area (upper slopes), in combination with other disturbance factors such as animal grazing, could have prevented the expansion of deciduous forest species from the relatively undisturbed lower slopes and valleys into the upper parts of the hill. Such local deforestation may explain the discrepancy between the pollen (regional signal) and charcoal (local signal) records of soil PRD-2.

For palaeo-wildfires in anthropisised landscapes, it is very difficult to eliminate the possibility of natural causes (Stewart, 1956), because the ignition trigger is unknown and a chemical distinction cannot be made between BC from natural wildfires and BC from fires ignited, deliberately or not, by past societies. As a consequence, the assessment of the potential role of human populations in a palaeofire regime relies on indirect indications. For the present study, a set of indirect evidence strongly points towards a significant anthropic influence in the fire regime: (1) From the pollen spectra, the presence of synanthropic pollen (*Urtica dioica* and *Plantago lanceolata*) in most of the samples of soil PRD-2, in combination with the presence of the non-pollen palynomorph (NPP) *Sordaria* Type 55A, proved that at least from 6000 cal BP onwards, the area was subjected to grazing disturbance, which very likely reflects the use of the area for livestock breeding (Rösch, 2000; López-Sáez et al., 2003; van Geel et al., 2003). For this purpose, fire would have been applied to clear the land. Earlier forest clearance phases (7000–6500 cal BP) may have aimed at creating pasture grounds for hunting, since they had occurred in pre-Neolithic contexts, when agriculture and livestock breeding were not yet in use. (2) The most significant episodes of accelerated environmental degradation coincide with cultural change not only in NW Spain but also in other parts of Europe and beyond. Analogous with the fire history reconstructions presented here, there is a vast body of evidence of increased burning frequencies in Western and Central Europe

since ca. 6000 cal BP (e.g. Clark et al., 1989; Carcaillet, 1998; Carrión and van Geel, 1999; Tinner et al., 1999; Gerlach et al., 2006) and plentiful proof (above all the simultaneous arrival of cereal pollen) for an anthropogenic cause is available (reviewed by Carcaillet et al., 2002). Although in the Rock Art park itself no evidence of agriculture was found, cereal pollen and seeds were detected in Campo Lameiro since 2700 cal BP and, on a regional scale, there is unequivocal evidence of generalised agricultural practices in NW Spain since ca. 6000 cal BP. The practice of animal husbandry instead of crop cultivation may explain the lack of pollen signal from cereals in the soils. It must be said though, that the use of fire for vegetation clearing may have had many other motives such as improving visibility around the petroglyphs, obviously impossible to detect using SOM fingerprinting. (3) Periods of climate amelioration, which would favour the expansion of forest communities, are not reflected as such in the soils studied, suggesting that non-climatic factors were involved in the burning regime. (4) It is difficult to imagine a small area being burned so frequently to produce a several meters thick blanket of BC-rich material from natural fires alone, especially when considering the local character of the fires. (5) On-site evidence of past societies (e.g. the concentration of rock art, remains of hut structures and the nearby presence of hillforts) suggest that the study area was strongly anthropisised since at least the Bronze Age or Late Neolithic.

Episodes of accelerated forest retreat occurred around 7000–6500 cal BP, 5700–5300 cal BP[6], 4000–3500 cal BP, 3000–2000 cal BP and 2000–1500 cal BP. The second and fourth of these episodes were probably the strongest in terms of vegetation change. These periods coincide with both major cultural shifts and climatic deterioration: (i) approximately 6000–5500 cal BP the widespread adoption of a Neolithic agropastoral productive system replacing hunter-gatherer strategies in the Atlantic façade roughly coincided with the onset of Neoglaciation (cooler and drier than the preceding Holocene Thermal Maximum period) and (ii) between 2000 and 1500 cal BP, the Roman and Germanic periods, also corresponding to the end of the Roman Warm Period. These results fit well in the accumulating body of indirect evidence of feedback mechanisms between climatic change, human impact and environmental degradation (e.g. Berglund, 2003; Martínez Cortizas et al., 2009; López-Merino et al., 2010). The other periods of environmental degradation do not coincide with known periods of climatic change: the period between 7000 and 6500 cal BP falls under the climatically favourable Holocene Thermal Maximum (or Atlantic period) and the period between 3000–2000 cal BP (Subatlantic) was

[6] The time frame of the Neolithic event of accelerated forest retreat varies throughout this thesis because of differences in the age estimation for this period in the different soils. For example, it was detected in soils PRD-1 and PRD-2 around 6000–5500 cal BP, while this episode was not detected in soil PRD-4 and for the anthracological study based on all five PRD soils (Manuscript 8), the period was more evident in the 5500–5000 cal BP interval than in that between 6000 and 5500 cal BP. Combined evidence suggests that this period could best be assigned between 5700 and 5300 cal BP.

climatically suitable for the development of deciduous forest, despite a short-lived cold and dry spell ca. 2800 cal BP. These episodes of environmental degradation may therefore be linked to human activities independent of climatic change: Late Epipalaeolithic/Mesolithic advanced hunting strategies and perhaps early pastoral activities (7000–6500 cal BP event) and Iron Age population growth and increased pressure exerted on the landscape (3000–2000 cal BP). The general picture is that climatic deterioration, in this study mainly following the Holocene Thermal Maximum (ca. 5500 cal BP) and the Roman Warm Period (ca. 1700 cal BP), mitigated the regenerative capacity of the vegetation thereby exacerbating the impact of human disturbance (fire and grazing), causing environmental degradation (reflected by erosion, acidification and deforestation). Thus, the destruction of deciduous forest in NW Spain is intimately associated with human intervention by the action of burning, probably since at least the Neolithic, eventually giving rise to the present-day cultural shrubland. It remains extremely difficult to quantify the relative impact of climatic change and human activities.

In the traditional agropastoral system of NW Spain, a clear division can be made between land use at *o monte* and the valleys and lower slopes. Intensive and permanent agricultural practices were concentrated in valleys and lower slopes. Two main approaches can be distinguished for land use at *o monte*. In the first approach, emphasis is on supplementary crop production following a slash-and-burn regime locally known as *roza* or *estivada*. In brief, shrub vegetation is cut/unrooted, dried in-situ, burnt, the ashes spread, the land cultivated and several years later abandoned to regenerate the soil under shrub vegetation, after which the cycle (10–15 yrs) is repeated (Bouhier, 1979; Balboa, 1990). In the second approach, the shrubs themselves are exploited for fuel (wood/charcoal), livestock fodder and/or organic fertiliser (details in Balboa, 1990). When used as organic fertiliser, the shrubs are implemented as stable bedding, after which the manure-enriched residues are applied to the cultivated soils in the valleys (e.g. Criado Boado, 1989). The pivotal role of N-fixating Fabaceae shrubs, especially *U. europeaus*, in maintaining fertile cultivated soils is illustrated by the fact that their seeds were actually sown (Bouhier, 1979). Moreover, *U. europeaus* shrubland was regularly rejuvenated by the use of fire to maintain monospecific shrub communities. Hence, in both approaches fire is a crucial element of recursive land clearance. The indications of a continuous and long-term prehistoric anthropogenic fire regime at *o monte* suggests that the continuous use of fire for vegetation clearing at *o monte* was inherited from Neolithic societies. Additionally, the early focus of forest regression at *o monte*, with downslope vegetation largely unaffected, suggests that the profound division between land use strategies at *o monte* and the valleys and lower slopes may have initiated already in the Neolithic. This would imply that the so-called fire culture and fire landscape of NW Spain had slowly evolved at a millennial time scale.

Obviously, the area was also exploited for resources such as dead and alive wood for domestic fires and charcoal production (necessary for metal working), timber (construction), food (e.g. fruits and mushrooms), utensils, etc. Forest deterioration had probably little impact on the availability of these resources because the lower slopes and valleys were only slightly affected. Other activities such as hunting (deduced from rock art motifs), trade, recreation or ritual practices (Bradley et al., 1995; Bradley and Fábregas Valcarce, 1998; Santos Estévez, 2005) could not be witnessed from the proxies used here either.

The current shrubland of *o monte* in the coastal areas of NW Spain is strongly controlled by Fabaceae (especially gorse and broom) while *E. arborea* is marginal. It is hypothesised that this reflects a cultural change that initiated at least a few hundred years ago when Fabaceae species came to be preferred over other shrub species because of their high nutritional value (N fixation) and fast growth. Before this shift *E. arborea* shrubland was possibly preferred because of the excellent charcoal it produces for fire kindling (domestic fires, metallurgy) (Martín Seijo, 2006) in combination with its strong natural capacity to colonise nutrient-depleted and fire- and grazing-afflicted areas. Since the second half of the 19th century and especially during the last 60 years, the traditional use of Fabaceae-dung mixtures on the agricultural fields in the valleys has been largely (but not completely) abandoned because of the use of inorganic fertilisers in combination with progressive emigration from the rural areas, reforestation policies and partition of the rural commons (Balboa, 1990; Bauer, 2005). The shrub communities at *o monte* are now left unused or replaced by pine and eucalyptus plantations, which are considered economically more feasible and require less labour from the owner (a necessary shift because of the exodus from the rural areas) (Marey, 2003). Consequently, rural villages, often found at the lower boundary of *o monte*, are nowadays surrounded by tree plantations and abandoned shrubland. Similar to other regions in Europe (Vos and Meekes, 1999; Terluin, 2003), the cultural and socio-economic role of the shrublands of rural NW Spain is disappearing. It is perhaps emblematic of the situation that current incentives in the Rock Art Park of Campo Lameiro aim at recolonisation by *Quercus* sp., apparently ignoring the possibility that burning the area (by the same societies that created the rock art) had been a cornerstone of land use management in NW Spain since Neolithic times and should thus be considered as part of our cultural heritage.

2.4 Conclusions

1. The thick organic matter-rich colluvial soils of NW Spain (Atlantic rankers), which formed as a result of Holocene slope transport processes, might well contain large amounts of BC from palaeofires, not only as large charcoal fragments (as was frequently reported) but also as finely divided and amorphous, largely NaOH-extractable material, as appeared to be the case for the soils of the study area. Therefore, BC may be a major agent in the pedogenesis of these soils. Furthermore, the abundance of BC may be responsible for the deep dark colour and explain the high resistance of the SOM against biological degradation, in combination with occlusion and the traditional sorptive preservation mechanisms. The indirect evidence of human influence in the fire regime that created these soils implies that the Atlantic rankers have an anthropogenic character.

2. Upon long-term burial, BC becomes increasingly oxidised, depolymerised, depolyaromatised, fractionated (on a macrostructural scale) and incorporated in the fine fabric of the soils studied here. The results presented suggest significant alteration of BC on the millennial scale. The difficulties in recognising amorphous and degraded BC without application of advanced molecular characterisation techniques explains why fire (thermal modification) was hitherto ignored as a major cause of SOM stability in Atlantic rankers.

3. In the study area, local deforestation and shrubland expansion started already ca. 7000 cal BP and accelerated since ca. 6000–5500 cal BP. In all likelihood, past societies used fire to clear the land and facilitate animal grazing, but climate deterioration after the Holocene Thermal Maximum and Roman Warm Period may have catalysed human inpact on the vegetation patterns. Fabaceae and Ericaceae shrubland communities first colonised the upper slopes of the hill and then probably expanded into the lower areas. The deciduous forest never completely recovered after the phases of forest retreat (ca. 7000–6500 cal BP, 5700–5300 cal BP, 4000–3500 cal BP, 3000–2000 cal BP and 2000–1500 cal BP) because of the intense burning and grazing disturbance regime imposed. This process might reflect the formation of the traditional dual landscape that can still be observed nowadays: shrubland and pasture grounds at *o monte* and cultivated land and some fragmented remains of deciduous forest in the valleys. If this proves correct, the roots of the *o monte* land use, including slash-and-burn practices and extensive pastoralism, may date back to the Neolithic and perhaps even Late Epipalaeolithic/Mesolithic period.

2.5 Recommendations for future research

1. Determine whether BC makes up a significant proportion of SOM in the Atlantic rankers from NW Spain. If results appear affirmative, that would be a strong indication that the reseach performed in Campo Lameiro (this thesis) can be extrapolated to other areas of NW Spain. Combining toponomical analysis (by contrasting topynyms related to fire with those related to oak) and SOM characterisation (BC content) of buried soils may be a promising approach in this context.
2. Study the role of charcoalphyllic fungi (e.g. *Cenococcum geophilum*) in SOM degradation in Atlantic rankers.
3. Analysis of the spatial dynamics of the fire-induced destruction of deciduous forest using pollen and charcoal records from colluvial soils and radiocarbon dating. Such an approach may provide information on the demographical distribution of past societies, on the origin of the division in land use at the upper slopes and valleys/lower slopes and on the expansion of manuring techniques in the Galician traditional agricultural system.
4. Develop methodologies to obtain more reliable chronologies from colluvial soils without radically increasing the number of radiocarbon measurements (see e.g. Martínez-Cortizas et al., *in press*). This will allow for narrowing down the time-range of climate, vegetation and fire regime change, thereby deconvoluting phases of change that are now pin-pointed at the ~500 yr scale, and better understand their causes through enhanced comparative analysis between methods. Such an attempt may produce fire frequency models and therefore a more thorough understanding of fire-vegetation dynamics and slash-and-burn practices.
5. The possibilities of molecular identification and characterisation of BC by pyrolysis-GC/MS need to be explored further, by analysis of a wide range of thoroughly characterised BC specimen from different sources, different ages and different levels of thermal modification. In addition, a better understanding of the pyrolysis reactions and subsequent recombinations is urgently needed, and an attempt must be made to improve the capacity of pyrolysis-GC/MS in quantifying the proportion of BC in SOM admixtures.
6. The possibilities of pyrolysis-GC/MS BC to detect uncharred material, to determine the degree of thermal impact and to monitor ageing processes in the soil environment offer great possibilities for agronomical studies involving implementation of biochar to improve soil fertility, limit soil degradation and sequester C in slow-cycling pools. Pyrolysis-GC/MS provides rapid and relatively cheap screening of biochar properties (see Schnitzer et al., 2007; Calvelo Pereira et al., 2010)
7. Pyrolysis-GC/MS may be useful to identify and characterise thermally

modified organic matter from archaeological materials (charred organic matter in potsherds, charred food residues, etc.) (e.g. Oudemans and Boon, 1991).

8. Anthracological and palynological analyses of a charcoal-rich Atlantic ranker with a high resolution and no hiatuses for the last ca. 1500 yrs may provide useful information on the shift from *Erica arborea*- to Fabaceae-dominated shrubland, which may represent the onset of using biomass from *o monte* as an organic fertiliser for cultivated soils downslope.

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PART B

LIST OF MANUSCRIPTS

Manuscript 1
Kaal, J., Martínez Cortizas, A., Buurman, P., Criado Boado, F., 2008. 8000 years of black carbon accumulation in a colluvial soil from NW Spain. *Quaternary Research* 69, 56-61.

Manuscript 2
Kaal, J., Martínez Cortizas, A., Nierop, K.G.J., Buurman, P., 2008. A detailed pyrolysis-GC/MS analysis of a black carbon-rich acidic colluvial soil (Atlantic ranker) from NW Spain. *Applied Geochemistry* 23, 2395-2405.

Manuscript 3
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Manuscript 4
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Manuscript 5
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Manuscript 6
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Manuscript 7
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Manuscript 8
Kaal, J., Carrión, Y., Asouti, E., Martín Seijo, M., Costa Casais, M., Martínez Cortizas, A., Criado Boado, F., *in press*. Long-term deforestation in NW Spain: Linking the Holocene fire history to vegetation change and human activities. *Quaternary Science Reviews,* doi: 10.1016/j.quascirev.2010.10.006.

MANUSCRIPT 1

8000 years of black carbon accumulation in a colluvial soil from NW Spain.

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Short Paper

8000 yr of black carbon accumulation in a colluvial soil from NW Spain

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Abstract

Analytical pyrolysis-GC/MS and solid-state ^{13}C NMR (nuclear magnetic resonance) were applied to the NaOH-extractable organic matter fraction of a colluvial soil from Galicia (NW Spain) that represents more than 8500 yr of accumulation. While molecular indicators of vegetation change were looked for, it seemed likely that any such signal was disturbed by the intense fire regime of the area. This conclusion was drawn from (1) the presence of three charcoal layers, (2) the high proportion of aryl C in NMR spectra (non-quantitative) and (3) the prevalence of benzenes and polycyclic aromatic hydrocarbons (PAHs) in the chromatograms (38±6% of total identified peak area), also in charcoal-poor samples. If this conclusion is accurate, the area has been subjected to burning episodes for at least 8000 yr. Additionally, the results indicate that biomass burning residues (black carbon; BC) may become NaOH extractable after long periods of degradation in mineral soil. These results add to our knowledge of the long-term fate of BC in soil, which is a potential agent in the global C cycle.

Keywords: Fire record; Black carbon; Pyrolysis-GC/MS

Introduction

Black carbon (BC) is the product of incomplete combustion of organic matter. It is a continuum of highly aromatic components ranging from weakly charred plant material through charcoal to soot. Black carbon is among the most recalcitrant terrestrial organic matter pools on Earth, and therefore potentially important in global C cycling (Goldberg, 1985). Nonetheless, owing to the chemical and physical diversity of BC and the related lack of a widely accepted quantification technique, the concentration and fate of BC in terrestrial soils are poorly understood (Schmidt and Noack, 2000). Degradation of BC creates problems in palaeorecords. For instance, while charring involves the loss of carboxylic functional groups (Almendros et al., 1992), the BC formed is susceptible to rapid oxidative degradation in the soil environment (Knicker et al., 2006). Consequently, the oxidation products of BC are highly aromatic carboxylated structures that are chemically similar to highly aromatic humic substances (e.g. Kumada, 1983; Haumaier and Zech, 1995; Shindo et al., 2004). The lack of straightforward evidence of a BC contribution to such humic substances is a significant limitation in our understanding of the role of fire in recalcitrant soil organic matter formation.

The Campo Lameiro area (Pontevedra, NW Spain) harbours one of the largest concentrations of rock art (petroglyphs) in the northwest of the Iberian Peninsula. By means of the creation of the *Rock Art Park of Campo Lameiro*, it is designed to become a major tourist attraction. However, the history of the area is poorly understood due to the scarcity of archaeological remains encountered in the surrounding soil. The soils comprise several meters of up to more than 8500 yr old colluvium. Stone and charcoal layers in these soils are indicative of episodes of soil redistribution by erosion/accumulation, probably linked to forest fires (Costa Casais et al., in press). The parent rock, migmatitic granite, yields large amounts of poorly crystalline aluminum hydroxides ("active Al") upon weathering, that is thought to be responsible for the stabilisation and accumulation

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of organic matter through sorptive processes (Carballas et al., 1967). This feature is typical of the thick organic-rich colluvial soils of NW Spain, referred to as Atlantic rankers, "cryptopodzolic Podzols" and aluminic soils which sometimes exhibit andic properties (Duchaufour, 1982; Delvaux et al., 2004; García-Rodeja et al., 2004).

Chemical fingerprinting of soil organic matter, using pyrolysis-GC/MS, did not prove to be useful for tracing vegetation changes in Campo Lameiro soil. Instead, results provide evidence of fires in the area throughout the Holocene. ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS NMR) was employed to support pyrolysis results. In addition, we aim at demonstrating the usefulness of CPMAS NMR and pyrolysis-GC/MS in studies concerning ancient BC, despite of inherent drawbacks: NMR underestimates the proportion of ^{13}C in condensed aromatic structures when CPMAS is used (Smernik et al., 2002) and an unknown fraction of BC may be non-pyrolysable or produce pyrolysis products that are not amenable to GC (Islas et al., 2002).

Materials and methods

The study site is located on an isolated hill at 320 m a.s.l. in NW Spain (U.T.M.: X: 538797; Y: 4710597). The parent rock is overlain by 40 cm of "inorganic" colluvium made of transported saprolite that dates back to the late Pleistocene–early Holocene ($C = 6.4 \pm 4.2$ g kg^{-1} soil), and 110 cm of strongly humic colluvium ($C = 72 \pm 34$ g kg^{-1} soil). Carbon and extractable Al contents are presented in Kaal et al. (in press), while a description of the geomorphology of the study site can be found in Costa Casais et al. (in press).

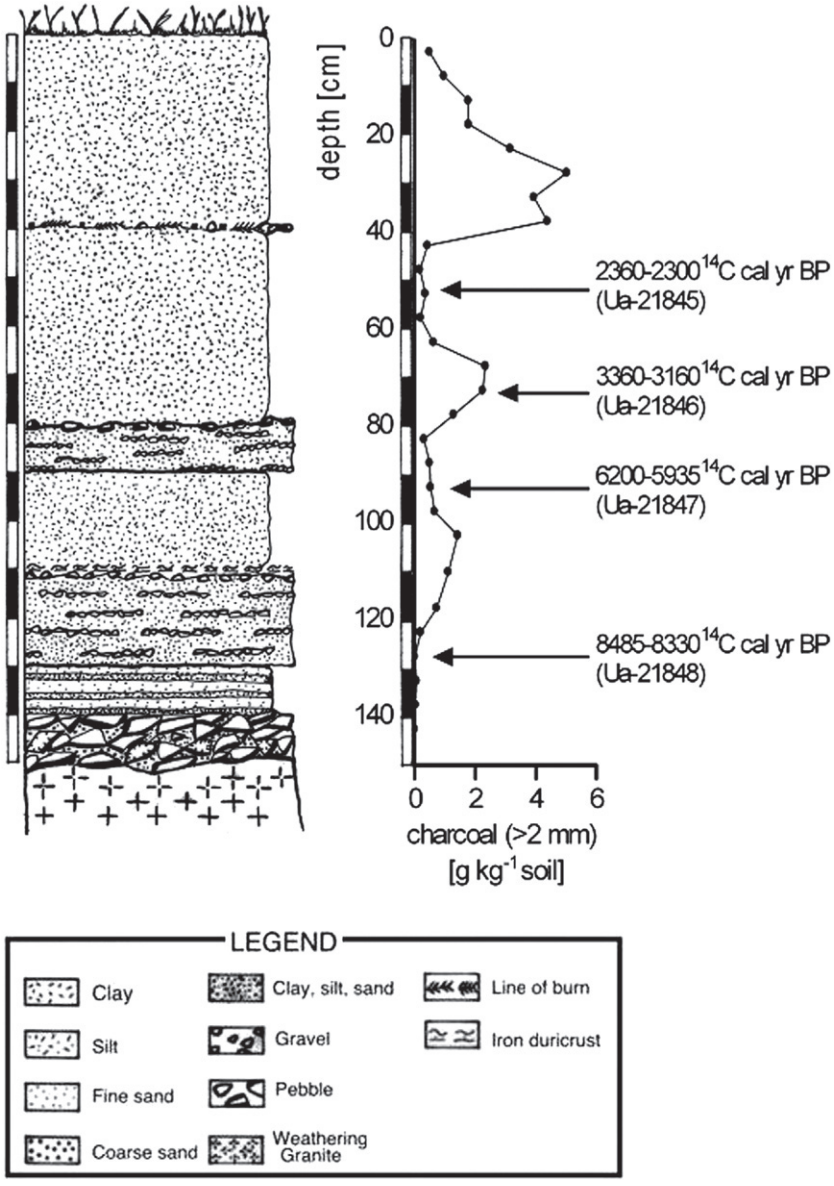

Figure 1. Soil profile (courtesy of M. Costa Casais), with to the right the macroscopic charcoal (>2 mm) profile with radiocarbon datings of the organic matter fraction (given as 2σ cal yr BP range).

A soil monolith from the surface to the base of the loose material at 145 cm was sliced into 5-cm sections to collect soil samples. An exception was made for the material between 105 and 115 cm, involving a stone layer, which was analysed as one sample. The material was air-dried and sieved over 2 mm to isolate the fine earth fraction. Macroscopic charcoal (>2 mm) was collected by means of wet sieving and weighed after drying. Figure 1 shows a representation of the soil profile, macroscopic charcoal content and radiocarbon dates of the organic matter fraction (Ångström Laboratory, Division of Ion Physics, ^{14}C-lab, Uppsala, Sweden).

Since pyrolysis-GC/MS of four selected soil samples (fine earth fraction, <2 mm) gave low-quality chromatograms and mass spectra, soil organic matter was separated from the fine earth fraction by extraction with 0.1 M NaOH for 5 min (twice) and water (3–5 times, until the supernatant was colourless) for further analysis (Nierop et al., 2001). Decanting of extracts was preceded by centrifugation at ~1000×*g* for 15 min. Extracts were then combined and acidified to pH 1.5–2.0 with HF/HCl (0.3/0.1 M), gently manipulated through a 63-μm mesh-size sieve to remove fine roots and buoyant smaller (63 μm–2 mm) charcoals, dialysed against distilled water and freeze-dried. The fine roots and the 63-μm to 2-mm charcoals accounted for a small yet undetermined proportion of non-extractable C and were omitted from analysis. Extraction yields were 82±12% of total C, as estimated from the difference of C content of the residues and that of the sample prior to extraction. The organic matter species discussed here are thus the NaOH-extractable fraction (2–123 g kg^{-1} soil; possibly containing some particulate matter <63 μm) and charcoals >2 mm (up to 50 g kg^{-1} soil; Fig. 1).

The NaOH-extractable organic matter was pyrolysed using a Curie-Point pyrolyser (600 °C) connected to a Carlo Erba GC 8000 gas chromatograph. The pyrolysis products were separated on a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51b (film thickness 0.40 μm), with helium as the carrier gas. The initial oven temperature was 40 °C, the heating rate 7 °C min^{-1}. The final temperature of 320 °C was maintained for 20 min. The GC column was connected to a Fisons MD 800 mass spectrometer (mass range *m*/*z* 45–650, cycle time 1 s). Replicates were obtained for two samples only.

The 94 pyrolysis products used for the quantification accounted for all major peaks in the total ion current. These compounds were generally quantified using the two major fragment ions. Relative response factors were assumed to be unity, which means the results are only semi-quantitative. The compounds were grouped according to their probable origin into the following component classes: benzenes *sensu lato* (benzene, C_1- and C_2-benzenes, naphthalene, C_1-naphthalene, benzofuran, dibenzofuran, biphenyl, anthracene/phenanthrene, fluorene and pyrene/fluoranthene), carbohydrates (acetic acid, 2-methylfuran, 2H-furan-3-one, 3/2-furaldehyde, 5-methyl-2-furaldehyde and levoglucosan), lipids (C_{10}-C_{33}-alkanes, C_{11}-C_{28}-alkenes, C_3-C_{20}-alkylbenzenes and a C_3-naphthalene), phenols (phenol and methylphenols), N-compounds (pyrrole, 3-methylpyrrole, diketodipyrrole, indole, pyridine, 2- and 3-methylpyridine, benzonitrile and (iso)quinoline) and lignins (guaiacol and 4-vinylguaiacol). The C_3-C_{20}-alkylbenzenes and the C_3-naphthalene showed concentration profiles that were similar to that of the lipid markers and were not found among the products of thermally assisted hydrolysis and methylation (THM; this technique can be envisaged as pyrolysis-GC/MS with preliminary addition of a methylating agent to protect functional groups from secondary pyrolysis reactions; Challinor, 2001) of selected samples (unpublished results). Therefore, these pyrolysis products were assumed to be cyclisation products of lipids (Saiz-Jiménez, 1995). We focus on the contributions of component classes rather than individual pyrolysis products to facilitate a comprehensive discussion.

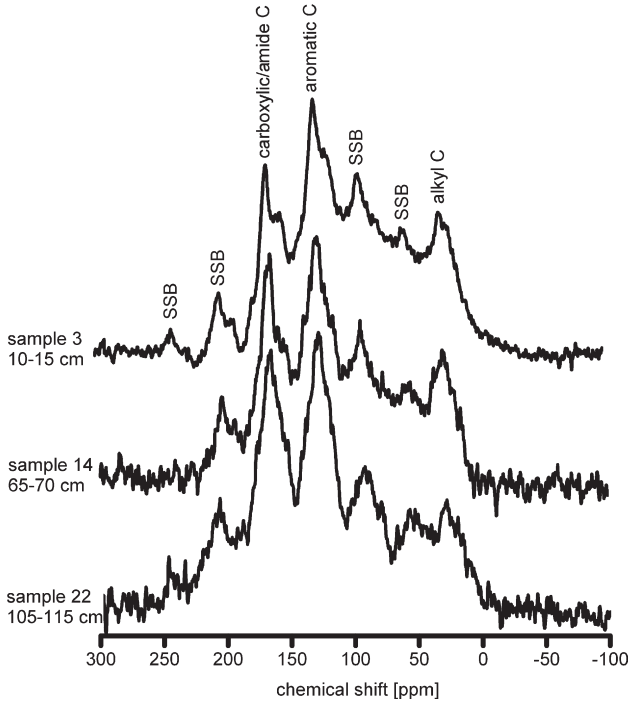

Figure 2. Solid-state ^{13}C CPMAS NMR spectroscopy of selected samples. Note the dominance of aromatic (128 ppm) and carboxyl/amide C (166 ppm). Most other peaks were not assigned due to possible overlap with spinning side bands (SSB; see text).

Solid-state ^{13}C CPMAS NMR of five selected samples of extractable organic matter was performed on an Inova 750 MHz spectrometer (Varian Inc., Palo Alto, CA, USA). Contact time was set as 1 ms, recycle delay was 1 ms and the spinning rate 7 kHz. Fourier transformation using a line broadening of 60 Hz was applied to the free induction decay files prior to manual phase and baseline corrections.

Results

The NMR spectra are distorted by significant spinning side bands (SSB) at ±74 ppm of the parent signals of aromatic (130 ppm) and carboxylic C (166 ppm; possibly including some amide C). The high degree of side-spinning is caused by the dominance of aromatic and carboxylic C (Fig. 2), which are most prone to side-spinning (Conte et al., 2004), and the high energy of the spectrometer. Although SSB can normally be easily mathematically relocated to their parent resonance, the

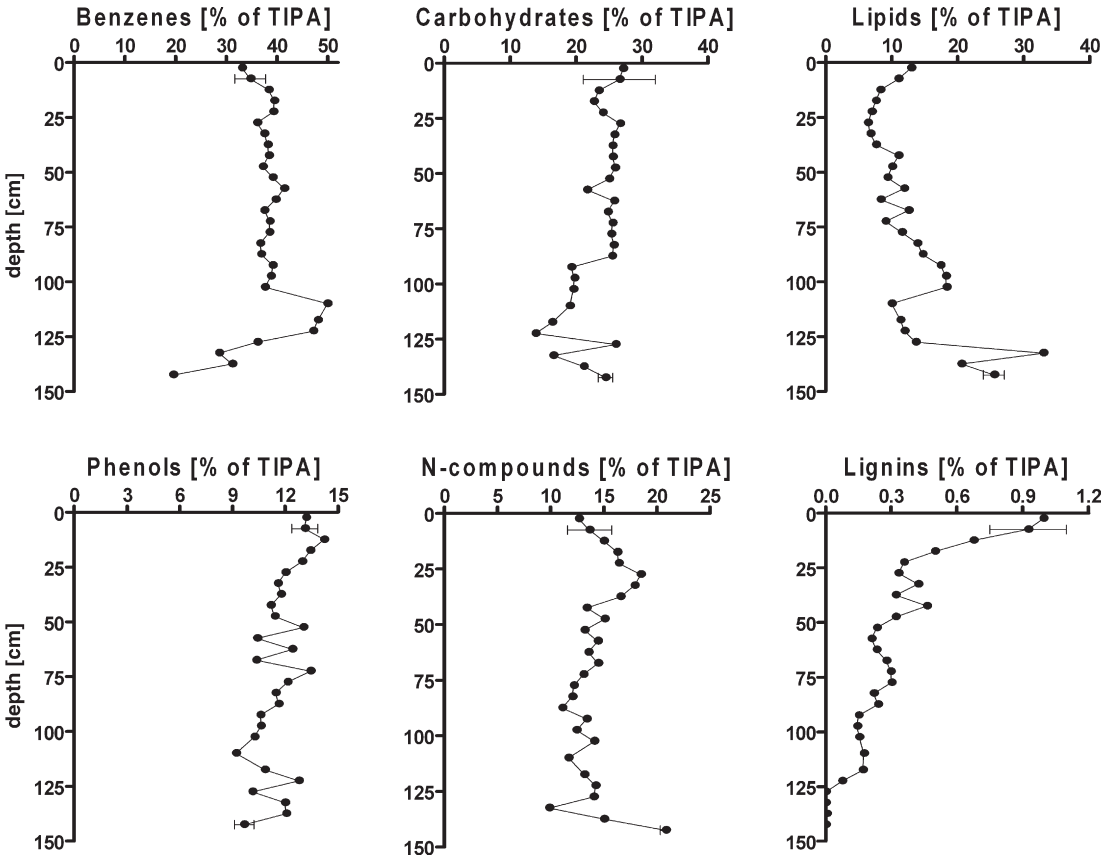

Figure 3. Component class distribution of quantified pyrolysis-GC/MS chromatograms, expressed as percentage of total identified peak area (TIPA). Note the differences in *y*-axis scaling. Error bars represent the standard error of the mean of duplicates (of two samples only).

SSB seem to have significant contributions to the remaining chemical shift regions, especially to those of di-*O*-alkyl and *O*-alkyl C (by carboxyl SSB) and methoxyl/*N*-alkyl C (by aromatic SSB), while the second order SSB of carboxyl C may even bias methyl C estimations (at 20 ppm). Hence, these results are not quantitative and serve only as evidence of the unusually large contribution of aromatic and carboxylic C.

The pyrolysis component class distribution confirms the large quantity of benzenes (Fig. 3). Three samples in the lower part of the profile display a benzenes contribution approaching 50% of total identified peak area. Carbohydrates have a significant contribution, even in the oldest samples at the bottom of the profile. The contribution of levoglucosan is 2.5% at the surface but it disappears towards the bottom of the profile ($r^2=0.75$, $P<0.001$, $n=30$; data not shown). The remaining carbohydrate markers are essentially furans (including furfurals), i.e. heterocyclic aromatic compounds. The lipid component class is dominated by *n*-alkane/alkene doublets. Lipids increase with depth ($r^2=0.50$, $P<0.001$, $n=30$) and thus age. Major negative excursions from this depth trend coincide with elevated macroscopic charcoal contents ($r^2=0.30$, $P<0.01$, $n=30$). Nitrogen-containing pyrolysis products are abundant (14.4±2.6%), despite of the poor observability of proteinaceous structures in complex mixtures using conventional pyrolysis-GC/MS (Chiavari and Galletti, 1992). Phenols show a small gradual decrease with depth. The soil is virtually devoid of lignin markers (0.30±0.28%). The lignin signature declines exponentially with depth.

Discussion and conclusions

As shown by ^{13}C CPMAS NMR, the main features of the organic matter are the preponderance of aromatic and carboxylic C. Using pyrolysis-GC/MS, benzenes are also the main component class, but pyrolysis products with carboxylic groups are scarce. The latter is presumably due to decarboxylation during the pyrolysis step (Martín et al., 1994) or the poor chromatographic properties of polar compounds in a non-polar GC column (Dignac et al., 2006). Indeed, preliminary experiments using THM showed large peaks of the methyl esters of benzenecarboxylic acids with up to six carboxylic groups. We believe that the benzenes, of which an unknown fraction is heavily carboxylated, represents the pyrolysis of partially oxidised BC.

One explanation for the inverse relation between the contribution of NaOH-extractable compounds yielding aliphatic pyrolysis products and macroscopic charcoal content is the selective consumption of lipid biomolecules during a fire. The effect of fire on lipids is highly variable, and Fernández et al. (2001) inferred that the lipid fraction may consist of a thermally labile and a fire-resistant fraction.

The N-containing pyrolysis products were mainly benzonitrile and heterocyclic aromatic N-compounds (92±3% of the total contribution of N-compounds), which are reportedly associated with charring (Alcañiz et al., 1994; Almendros et al., 2003; Knicker et al., 2005). Lignin markers are virtually absent

(<1.0%), which can be attributed to the loss of the methoxyl functionality during charring (González-Pérez et al., 2004), confirmed by the weak signal of methoxyl C (ca. 45–60 ppm) in the ^{13}C NMR spectra.

From the pyrolysis-GC/MS analyses, the carbohydrates were mainly furans. Although these products may form upon the pyrolysis of intact cellulose, the small contribution of the latter's dominant pyrolysis product, i.e. levoglucosan (Poirier et al., 2005), indicates that the carbohydrates had lost most of their (di-)*O*-alkyl C groups. Therefore, the carbohydrate compartment is strongly degraded. The extensive rearrangement of carbohydrate structures to furan-based (hence aromatic) structures is a well-known product of charring when analysed by pyrolysis-GC/MS (e.g. Pastorova et al., 1994) or ^{13}C NMR (Baldock and Smernik, 2002). Alternatively, the degraded state of the carbohydrate class indicates non-thermal (e.g. microbial) degradation. The decreasing levoglucosan contribution with depth very likely represents the decay of uncharred polysaccharide material.

Altogether, we consider the pyrolysis-GC/MS fingerprint indicative of the presence of large amounts of NaOH-extractable BC. We are not aware of any process other than charring to cause the accumulation of highly aromatic organic matter dominated by domains of benzenes and PAHs (38±6% of total identified peak area), heterocyclic N compounds and benzonitrile. The sum of these probably BC-derived pyrolysis products is 51±6%. This is of course only a rough estimate of BC content due to the possible BC origin of the furans and aforementioned drawbacks in the pyrolysis-GC/MS technique. We consider pyrolysis-GC/MS capable of assessing BC in NaOH-extractable organic matter, but obviously not for its quantification. CPMAS NMR and pyrolysis-GC/MS are more likely to under represent BC than overestimate its proportion because of the lack of protons for ^{1}H-^{13}C cross polarisation in condensed aromatic structures and the possible formation of a non-pyrolysable residue, respectively.

The pyrolysates of the samples from the bottom of the profile (125–145 cm) exhibit lowest benzenes (Fig. 3) and total aromaticity contributions (not shown), which may indicate the absence or a smaller contribution of BC to the organic matter. The sample taken at a depth of 125–130 cm was dated 8435–8330 cal yr BP. Therefore, we hypothesise that the area was subjected to at least 8000 yr of burning episodes.

Some studies in Galicia showed that charcoal layers coincide with periods of known human activity from the mid-Holocene onwards (Martínez Cortizas et al., 2005). Radiocarbon dating combined with pyrolysis-GC/MS suggests that also before that time (ca. 8000 BP and after), fire had an important effect on the soil and landscape evolution. Whether the fires were natural or produced by past societies has yet to be elucidated. Additionally, the abundance of highly aromatic organic matter in almost all samples indicates that the macroscopic charcoals provide an incomplete picture of the fire history.

Finally, the results invoke the question whether the large amount of "active Al" is responsible for the long-term stabilisation of the organic matter in the study area (see Introduction). A complementary cause is that the carboxylic groups on the intrinsically recalcitrant BC-derived organic matter, combined with its large surface area and porosity, allows it to undergo strong interactions with mineral phases, thereby further protecting the BC against biodegradation (Brodowski et al., 2005; Knicker et al., 2006). The sorptive interaction between heavily functionalised BC-derived recalcitrant organic matter and "active Al" could perfectly explain why thousands of years old material exhibits organic C contents of up to 14% in a humid temperate climate such as that of Galicia.

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MANUSCRIPT 2

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A detailed pyrolysis-GC/MS analysis of a black carbon-rich acidic colluvial soil (Atlantic ranker) from NW Spain

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ABSTRACT

Despite the potentially large contribution of black carbon (BC) to the recalcitrant soil organic matter pool, the molecular-level composition of aged BC has hardly been investigated. Pyrolysis-GC/MS, which provides structural information on complex mixtures of organic matter, was applied to the NaOH-extractable organic matter of an acidic colluvial soil (Atlantic ranker) sampled with high resolution (5 cm) that harbours a fire record of at least 8.5 ka. Additionally, 5 charcoal samples from selected soil layers were characterised using pyrolysis-GC/MS for comparison. Pyrolysis-GC/MS allowed distinguishing between BC and non-charred organic matter. It is argued that a large proportion of the polycyclic aromatic hydrocarbons (PAHs), benzenes and benzonitrile in the pyrolysates of the extractable organic matter, together accounting for 21–54% of total identified peak area, derived from BC. In charcoal samples, these compounds accounted for 60–98% of the pyrolysis products. The large quantity of BC in almost all samples suggested a key role of fire in Holocene soil evolution. The high C content of the soil (up to 136 g C kg^{-1} soil) may be attributed to the presence of recalcitrant organic C as BC, in addition to the sorptive preservation processes traditionally held responsible for long-term C storage in acid soils. Interactions between reactive Al hydroxides and BC could explain the longevity of BC in the soil. This work is the first thorough pyrolysis-GC/MS based study on ancient fire-affected organic matter.

1. Introduction

Incomplete combustion of fossil fuels, living biomass or soil litter leaves behind a solid residue that is referred to as black carbon (BC). Black C comprises a 'combustion continuum' encompassing slightly charred biomass, charcoal and soot (Masiello, 2004). In recent years, BC has been the focus of research because it may act as a significant C sink in terrestrial and aquatic environments (Seiler and Crutzen, 1980; Preston and Schmidt, 2006). While BC was initially thought to be immune to decay processes, it became clear that physical fractionation, microbial attack, chemical breakdown and humification act on BC just as they do on any other organic component in soil (Cohen-Ofri et al., 2006; Forbes et al., 2006) and that the accumulation of BC may require reactive soil minerals to protect it against degradation (Czimczik and Masiello, 2007). The chemical evolution of BC under the influence of these degradation processes is still enigmatical.

The fate of BC in the environment is difficult to unravel because its identification and quantification is not straightforward when occurring in combination with other forms of soil organic matter. A standardised method for BC assessment does not exist, which is attributable to the heterogeneity of the compounds it embodies (Hammes et al.,

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2007). Physical methods such as charcoal counts provide BC contents very different from those obtained by more complicated chemical approaches (Schmidt and Noack, 2000). Identifying BC is especially problematical when it had been subjected to long-term diagenetic transformation and incorporation into 'humic substances'. More specifically, BC becomes increasingly hard to distinguish from highly aromatic humic acids (Hatcher et al., 1989) through the development of functional groups over time, rendering identification and quantification of 'ancient' (>1 ka old) BC very difficult (Cohen-Ofri et al., 2006). Many authors suggested that BC may be the principal source of these so-called Type A humic acids (Haumaier and Zech, 1995; Skjemstad et al., 1996; Golchin et al., 1997; Schmidt et al., 1999; Kramer et al., 2004), so that distinction between the two would not be realistic.

Field and laboratory studies applying ^{13}C and ^{15}N NMR (nuclear magnetic resonance) indicate that the thermal modifications of organic matter during charring include dehydration, aromatisation, loss of methoxylic and carboxylic functional groups, condensation of carbohydrates into furan-like structures and enrichment of heterocyclic aromatic N-compounds (González-Pérez et al., 2004; Knicker et al., 2005). Although NMR offered the necessary framework for studying thermal alterations of organic matter, its capacity to provide structural information of complex mixtures is limited. Pyrolysis-GC/MS is an alternative approach that involves thermal degradation of biomolecules followed by identification of the pyrolysis products by GC/MS. One might expect that pyrolysis-GC/MS is impractical for BC analysis as it involves two stages of thermally-induced alterations (the fire itself and the pyrolysis step), and because an unknown fraction of BC may not be transformed to GC-amenable products during pyrolysis (Poirier et al., 2003; Rumpel et al., 2007). However, using pyrolysis-GC/MS the effects of heating on cellulose and lignin have been established (Pastorova et al., 1994; Knicker et al., 2005) and Naafs (2004) showed that the chemically recalcitrant fraction of an andic soil carried evidence of charring. Even though pyrolysis-GC/MS has additional drawbacks such as decarboxylation of aromatic acids and other rearrangements during the pyrolysis step, a good correlation with the ^{13}C NMR spectra from BC was reported by Pastorova et al. (1994). Despite the potential of pyrolysis-GC/MS to provide rapid molecular characterisation, pyrolysis-GC/MS is seldom applied to sediments carrying BC. In fact, pyrolysis-GC/MS was not even mentioned in a section on BC characterisation methods of a recent review (Preston and Schmidt, 2006).

In this paper pyrolysis-GC/MS results of 28 samples taken from a 1.5 m deep acid colluvial soil located in Campo Lameiro, NW Spain (Fig. 1), that contains three charcoal layers, are presented. These type of soils, which sometimes exhibit andic properties, are traditionally referred to as 'Atlantic rankers', but also as humiferous Atlantic soils, abortive or cryptopodzolic podzols and aluminic soils (Duchaufour, 1982; Delvaux et al., 2004; García-Rodeja et al., 2004). These thick blackish soils have a high organic matter content, which is thought to be protected from microbial degradation through the formation of organometallic complexes (Carballas et al., 1967, 1978). The soil studied here indeed contains significant amounts of organically bound poorly crystalline Al hydroxides (Kaal et al., 2008a). It represents at least 8.5 ka of colluviation. A summary of pyrolysis-GC/MS and ^{13}C NMR results of the NaOH-extractable organic matter from the soil can be found in Kaal et al. (2008b).

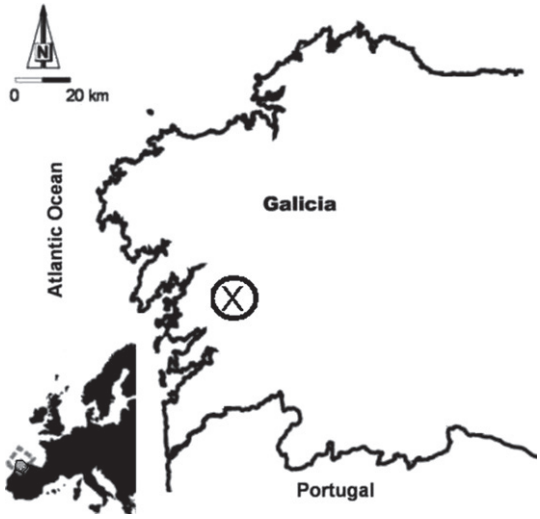

Fig. 1. Location of the study area.

The present study will (1) demonstrate the value of pyrolysis-GC/MS for BC studies by testing the hypothesis that a large fraction of the organic matter originates from BC and (2) discuss the accumulation of organic matter in acid colluvial soils in the light of abundant BC.

2. Experimental

2.1. Site description and sampling

The present climate of the Campo Lameiro area (Fig. 1) is mild and humid; average annual temperature is 15 °C (9 °C in winter and 21 °C in summer) with an annual precipitation of 1200 mm (concentrated in autumn and winter months) (Martínez Cortizas and Pérez Alberti, 1999).

The site is on an isolated hill at 320 m a.s.l., 25 km east from the Atlantic Ocean. The parent rock is migmatitic granite, on which 40 cm of inorganic colluviated saprolite (C content = 6.4 ± 4 g kg^{-1} soil) was deposited in the late Pleistocene-early Holocene (Fig. 2). This was followed by the deposition of 110 cm of strongly humic colluvium (C = 72 ± 35 g kg^{-1} soil), which constitutes the 'true' ranker. The colluvial phases are interrupted by three charcoal layers, i.e. unequivocal evidence of local wildfires, and several layers with coarse material reflecting accelerated erosion episodes. The Na-pyrophosphate-extractable Al concentration of the soil, which is a measure of organically bound Al, is 8.4 ± 4.9 g kg^{-1} soil and strongly correlated to total C content (r^2 = 0.89, P<0.001). The soil reaction (pH–H_2O) was 5.0 ± 0.2 and showed and increase with depth (r^2 = 0.88, P<0.001). Complete data and the methods used for obtaining them can be found in Kaal et al. (2008a).

Twenty-eight soil samples were collected at regular intervals of 5 cm until the base of the solum. The material

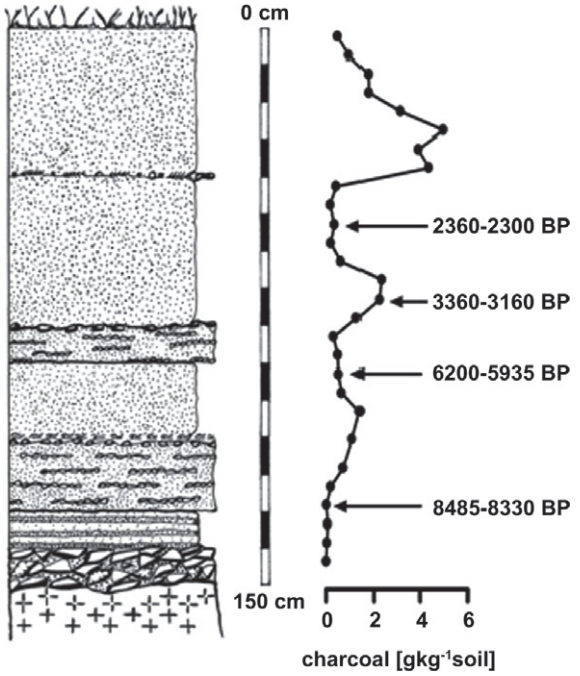

Fig. 2. Representation of the soil profile, showing stone layers and the line of burned soil at 40 cm. To the right, the macroscopic charcoal profile with radiocarbon ages (given as 2σ cal. a BP range).

was air-dried and sieved through 2 mm to separate the fine earth fraction. Macroscopic charcoal (>2 mm) was collected by means of wet sieving and weighed after drying. Charcoal content and radiocarbon ages of the organic matter (obtained at The Ångström Laboratory, Uppsala, Sweden) are given in Fig. 2.

2.2. Isolation of organic matter

Soil organic matter was separated from the fine earth fraction by extraction with 0.1 M NaOH (10 g soil:50 mL aqueous NaOH) (twice) and water (3–5 times, until the supernatant was colourless) (Nierop et al., 2001). Decanting of extracts was always preceded by centrifugation at ~1000*g* for 15 min. All extracts were combined and acidified to pH 1.5–2.0 with 4:1 HF/HCl solution. Next, the suspensions containing the extracted organic matter were gently manipulated through a 63 μm mesh-size sieve to remove buoyant fine roots and smaller charcoal (63 μm–2 mm). Subsequently, the suspensions were dialysed against distilled water and freeze-dried, producing a powder of extractable organic matter. Extraction yields for C were high, 81.5 ± 12% of total C, as calculated from elemental analyses of the residues and the untreated fine earth fraction, suggesting that the extractable fraction was representative of the soil organic matter.

2.3. Pyrolysis-GC/MS

The freeze-dried organic matter was pyrolysed using a Horizon Instruments Curie-Point pyrolyser (Curie-temperature of wire = 600 °C) connected to a Carlo Erba GC 8000 gas chromatograph. The pyrolysis products were separated on a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51b (film thickness 0.40 μm), with He as the carrier gas. The initial oven temperature was 40 °C and the heating rate was 7 °C min^{-1}. The final temperature of 320 °C was maintained for 20 min. The GC column was connected to a Fisons MD 800 mass spectrometer (mass range *m/z* 45–650, cycle time 1 s).

The 94 pyrolysis products used for the quantification (Appendix A) accounted for all major peaks in the total ion current (TIC). The 94 compounds were generally quantified on the two most abundant fragment ions using the quantification option in the MassLab 1.2.7 software. All peaks had to be checked manually due to differences in retention times and sometimes incorrect baseline estimations by the software. The compounds were grouped according to the probable origin into the following component classes: benzenes, carbohydrates, lipids, N-compounds, PAHs, phenols and lignins.

Benzenes: benzene, toluene, *p*-xylene, 1,2-dimethylbenzene (although perhaps 1,3-dimethylbenzene), ethylbenzene and styrene. A series of C_3–C_{20} alkylbenzenes was grouped with the lipids.

Carbohydrates: 3- and 2-furaldehyde (combined), 5-methyl-2-furaldehyde, 2-methylfuran, 2H-furan-3-one, acetic acid and levoglucosan. Low intensities of levoglucosenone were found in some samples but not taken into consideration.

Lipids: C_{10}–C_{28} alkane/alkene doublets, C_{29}–C_{31} alkanes and C_{33}-alkane. The concentration profiles of C_3–C_{20} alkylbenzenes and a C_3-naphthalene (probably propylnaphthalene) were very similar to those of the *n*-alkanes/alkenes, indicating that they are most likely secondary pyrolysis products of straight-chain fatty acids (Czechowski and Marcinkowski, 2006; Quénéa et al., 2006). These compounds were not found in the thermochemolysate of selected samples analysed by tetramethylammonium hydroxide (TMAH) thermochemolysis (data not shown), implying that methylation prior to pyrolysis inhibits the cyclisation of straight-chain aliphatics (Saiz-Jiménez, 1995). Adding these arenes to the lipid fraction yielded a total number of 60 lipid markers. Methylketones and C_{14}–C_{16} and C_{18} fatty acids were present but not suitable for quantification due to their small concentrations (methylketones) or poor chromatographic properties (fatty acids).

Nitrogen-compounds: pyrrole, 3-methylpyrrole, pyridine, 2- and 3-methylpyridine, benzonitrile, diketodipyrrole, indole and (iso)quinoline. A contribution of picolamine to the 3-methylpyrrole peak (*m/z* 80 + 81) cannot be excluded.

PAHs: naphthalene, 1- and 2-methylnaphthalene (poorly resolved and therefore combined), biphenyl, anthracene/phenanthrene, pyrene (perhaps with fluoranthene), and fluorene. Benzofuran and dibenzofuran, which are heterocyclic analogues of PAHs, were grouped with the PAHs. A C_3-naphthalene was grouped with the lipids (see above). Small peaks of 7H-benzo-C-fluorene could not be quantified.

Phenols: phenol and 2- and 4-methylphenol.

Lignins: guaiacol and 4-vinylguaiacol.

Duplicates obtained for samples 2 (5–10 cm) and 28 (140–145 cm) were alike (based on the pyrolysis product contributions: $n = 94$, $r^2 = 0.95$ and 0.98 for the duplicates of samples 2 and 28, respectively). The results presented for these samples are average values.

The collected macroscopic charcoal of 5 samples (3, 14, 15, 19 and 22) was finely ground, analysed by pyrolysis-GC/MS, and the pyrograms were quantified as described above for the NaOH-extractable fraction. Aliquots of acetone had to be added to the charcoal in order to obtain a good coating of the ferromagnetic wires.

Appendix A contains minimum, maximum and average contributions to the NaOH-extractable organic matter of the individual compounds, and their enrichment factors (EF) in the macroscopic charcoal:

$$\text{EF of compound } i = \frac{\text{proportion of compound } i \text{ in charcoals}}{\text{proportion of compound } i \text{ in NaOH} - \text{extractable organic matter}}$$

The pyrolysis-GC/MS dataset was quantitatively biased because each compound has a different extent of ionisation resulting in different relative response factors. Also, some compounds could not be accurately quantified (see above), some compounds may have been overlooked owing to co-elution with more abundant pyrolysis products, and many low molecular weight compounds have been disregarded due to elution in the non-deconvolutable first 2 min of scanning. Consequently, the results are at best semi-quantitative, but this does not inhibit a reliable comparison of the samples studied here or in other pyrolysis-GC/MS studies.

Factor analysis (SPSS 13.0) was applied to the large dataset obtained by pyrolysis-GC/MS. More specifically, clustering pyrolysis products using factor analysis assists in interpreting a compound of unknown macromolecular origin (Buurman et al., 2006). Factor analysis can be especially valuable for the interpretation of the pyrolysis-GC/MS fingerprint of material containing BC, since evidence of unambiguous pyrolysis markers of BC is missing.

3. Results and discussion

3.1. NaOH-extractable organic matter

The pyrolysates of the extracted organic matter were dominated by benzenes and other aromatic pyrolysis products. The benzenes component class accounted for 31 ± 6% of the total identified peak area (Fig. 3a). The benzenes content was lowest at the bottom of the soil (<20%), and increased to a maximum of 43% at 110 cm. This sample corresponded to a soil horizon rich in gravel and stones that was deposited somewhere between 6 and 8.5 ka BP. The benzenes contribution barely fluctuated above this stone line and thus did not respond to the major shifts in macroscopic charcoal content in the top meter. However, individual pyrolysis products of the benzene class varied considerably in the top 50 cm of the profile. Within this soil layer, the samples with highest macroscopic charcoal content (0.6 mg g^{-1} soil) showed a minimum contribution of pyrolysis products toluene and C_2-benzenes, and a maximum of benzene (Fig. 3a). The unusually large contribution of benzenes to the pyrograms in general is a first indication of the presence of significant amounts of BC (Naafs, 2004; Kaal et al., 2008b).

Carbohydrate markers were abundant (23 ± 4%), even in the oldest soil layers (Fig. 3b). The furaldehydes and acetic acid (Fig. 3b), which dominated the carbohydrate component class together with 2-methylfuran (not shown), had relatively small contributions from 90 to 135 cm (samples 19–24), which coincided with either high benzene or PAH contributions. Small contributions were observed for levoglucosan (<2.5%), a pyrolysis product of intact polysaccharide (Pastorova et al., 1994; Poirier et al., 2005) which is typically the principal pyrolysis product of unscathed cellulose (e.g. in peat or fresh litter). The contribution of levoglucosan declined in the top 20 cm, and then gradually disappeared towards the bottom of the profile (negative trend with depth: $r^2 = 0.75$, $P < 0.001$). The levoglucosan curve plausibly mirrors the degradation of primary (plant-derived) polysaccharides in the soil with age, and although levoglucosan can also be a biomarker of high-temperature combustion when applying GC/MS (Simoneit, 2002; Otto et al., 2006), the levoglucosan observed by pyrolysis-GC/MS originated from the pyrolysis of intact polysaccharides in the pyrolysis chamber. This is consistent with pyrolysis-GC/MS studies on cellulose chars (Boon et al., 1994; Pastorova et al., 1994), which showed that levoglucosan is mostly derived from non-charred material. The heterocyclic aromatic carbohydrate markers are more ambiguous with regard to a possible BC origin, because a lack of levoglucosan but high abundance of furan and furaldehydes can alternatively be explained by intense biological activity (Page et al., 2002).

Remarkably large amounts of PAHs were present in all pyrolysates (6.3 ± 1.8%) (Fig. 3c). Especially the higher molecular weight pyrolysis products anthracene and pyrene are strong evidence of charred organic matter (Naafs, 2004; Rumpel et al., 2007). The PAHs were inversely related to the carbohydrate component class ($r^2 = 0.74$, $P<0.001$), suggesting that carbohydrates formed the main source of PAHs. This is in agreement with laboratory studies showing that cellulose charred at temperatures above 310 °C produced a variety of PAHs upon pyrolysis (Pastorova et al., 1994). Consequently, the PAHs are probably a product formed during high-temperature fire events (Naafs, 2004).

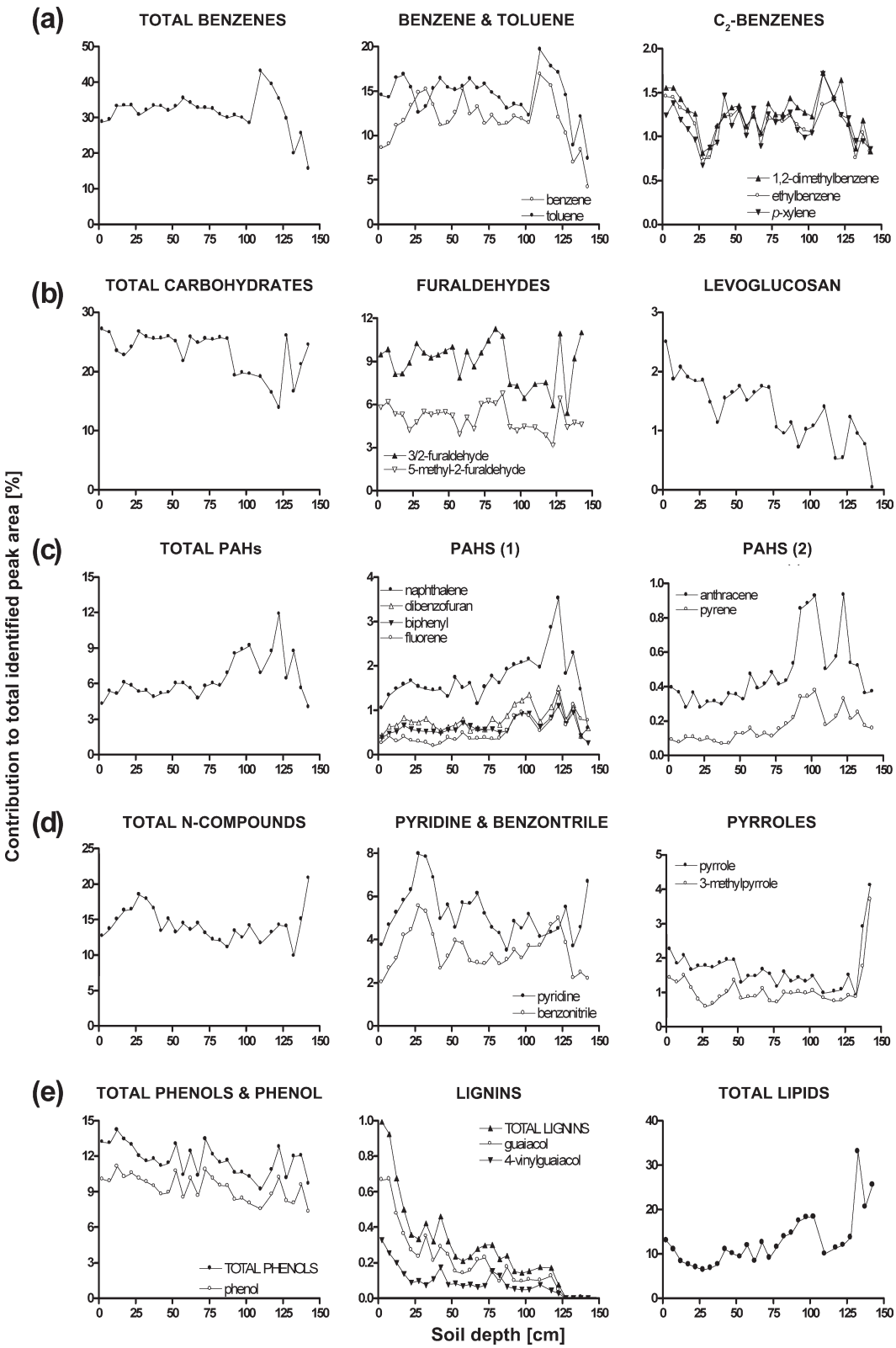

Fig. 3. Pyrolysis-GC/MS component class distributions and the depth profiles of selected individual pyrolysis products (in% of total identified peak area). Note the differences in *y*-axis scaling.

Although pyrolysis-GC/MS tends to underestimate the contribution of N-containing biomolecules (Chiavari and Galletti, 1992; Kaal et al., 2007), their pyrolysis products were abundant in all samples (14.4 ± 2.6%) (Fig. 3d). The observed N-compounds were benzonitrile and compounds that have N-substituted aromatic rings (pyrrole, 3-methylpyrrole, pyridine, 2-methylpyridine, 3-methylpyridine, indole, diketodipyrrole and (iso)quinoline). Pyrrole, 3-methylpyrrole, the methylpyridines and indole were negatively correlated with the benzenes class (r^2 = 0.26–0.61; for all, P<0.01), whereas benzonitrile was positively correlated to the benzenes (r^2 = 0.31; P<0.01). In the top 50 cm, which contain the youngest charcoal layer, benzonitrile and pyridine were enriched in the samples with highest charcoal content, while methylpyridines, indole, 3-methylpyrrole and diketodipyrrole showed a minimum in these samples, indicating an interesting shift within the N-compounds class upon this particular fire event. It should be noted that the organic matter may contain significant amounts of amide N in peptide structures, which are partially resistant to thermal treatment (Knicker et al., 1996), but rarely observed by pyrolysis-GC/MS of complex mixtures.

The precursors producing phenols upon pyrolysis (Fig. 3e) gradually declined from approximately 14% at the surface to 10% at the bottom of the profile (depth trend: r^2 = 0.40, P<0.001). Phenols do not originate from one specific source.

The contribution of lignin markers (Fig. 3e) was remarkably small (0.30 ± 0.28%) and declined with depth (r^2 = 0.76, P<0.001). The lack of lignin products can be explained by biodegradation or biomass burning, which eliminates their methoxyl groups (González-Vila et al., 2001; Almendros et al., 2003). Although lignin markers were scarce, lignin's biological or thermal degradation products may have acted as a significant source of the benzenes and phenols. (And perhaps some lignin was converted to PAHs during fire, although it was shown that the majority of the PAHs probably derive from carbohydrate structures.)

The total of lipid markers tended to increase with depth (r^2 = 0.51, P<0.001) from ca. 8 to 30% (Fig. 3e), reflecting the relative resistance against biodegradation of lipids (Baldock et al., 1997) or gradual neoformation of aliphatic geopolymers (de Leeuw et al., 2006).

When the origin of a given pyrolysis product is uncertain, factor analysis may aid in resolving its princi-

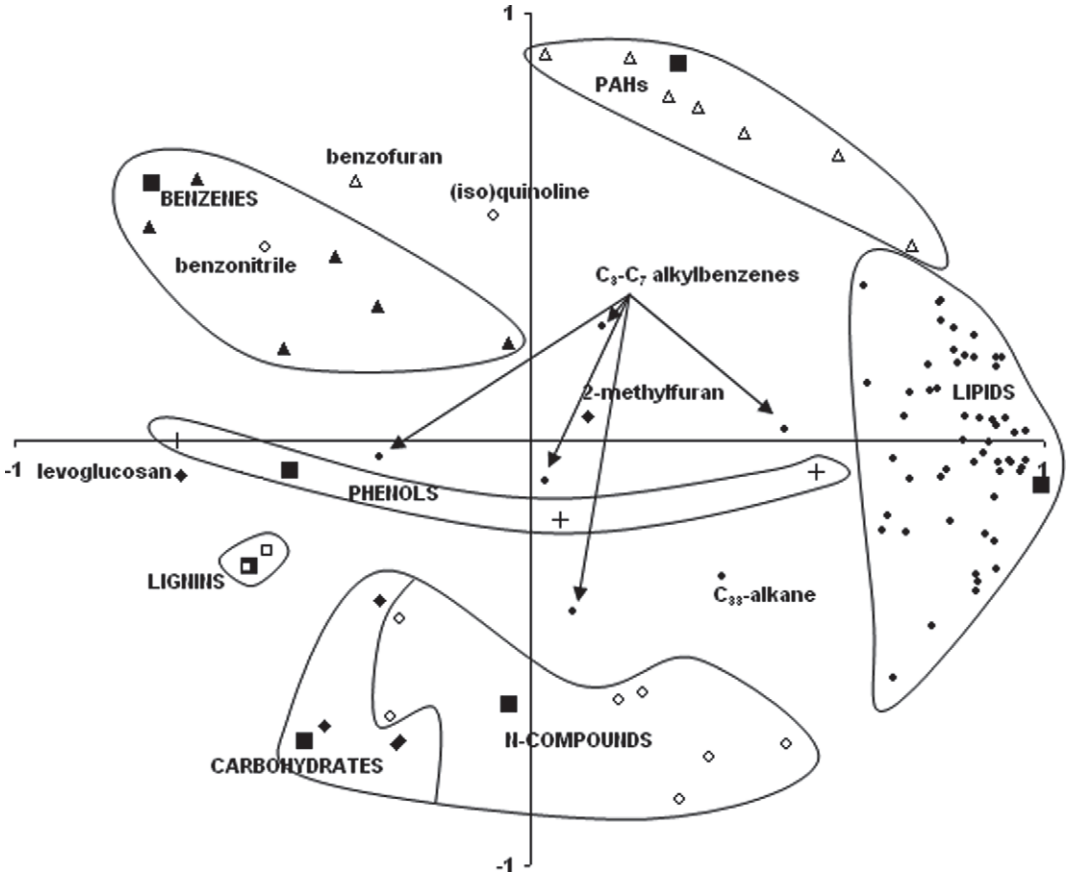

Fig. 4. Factor analysis of the component class distributions (■) and individual pyrolysis products: ▲ benzenes, Δ PAHs, ♦ carbohydrates, ○ N-compounds, ● lipids, + phenols, □ lignins.

pal source (Buurman et al., 2006). Fig. 4 shows the pyrolysis component classes and products in factor space. Factor 1 explained 46% of total variance, and Factor 2 15%. Factor 1 reflected the depth/age trend of the pyrolysis products, with those that showed a marked decrease with depth plotting on the negative side of F1 (e.g. levoglucosan and the lignin markers), while pyrolysis products of which the contribution increased had positive loadings on F1 (essentially the lipids). Factor 2 separated the heterocyclic aromatics (furans, furaldehydes and most N-compounds) from the benzenes, PAHs, benzonitrile and (iso)quinoline. This was probably the separation of the pyrolysis products of degraded organic matter (negative loading on F2) from the BC products (positive on F2). Benzonitrile plotted close to the benzenes and was clearly separated from the other N-compounds. Benzonitriles could have derived from thermal decomposition of aromatic amines (Schulten and Schnitzer, 1998) and Alcañiz et al. (1994) showed that heating of organic matter caused the accumulation of benzonitrile, naphthalene and other aromatic hydrocarbons. A BC-rich andic soil from Madeira also produced significant amounts of benzonitrile upon pyrolysis (Naafs, 2004). The authors believe that large amounts of benzonitrile in pyrolysates indicates the presence of pyrogenic C (and N). The clear separation of the pyrolysis products in factor space suggested that the pyrolysis products can indeed be subdivided in the markers of BC and non-charred primary and degraded organic matter. That the BC was released by NaOH solution can be explained by post-fire oxidation (functionalisation) in the soil, which increases its solubility (Haumaier and Zech, 1995).

3.2. Pyrolysis-GC/MS of macroscopic charcoal

As it appeared that the extractable organic matter carries signals of charring, 5 macroscopic charcoal assemblages (isolated from samples, 3, 14, 15, 19 and 22) were selected for pyrolysis-GC/MS to study the differences between extractable organic matter and charcoal composition. It appeared that the charcoals of samples 14, 15, 19 and 22 were dominated by benzenes (87 ± 6%, of which 91 ± 2% benzene), with minor contributions of PAHs (5.2 ± 0.3%), lipids (3.3 ± 2.4%), N-compounds (1.5 ± 0.9%, of which 87 ± 7% benzonitrile), carbohydrates (1.4 ± 2.1%), phenols (1.3 ± 0.6%) and lignins (0.05 ± 0.09%). Thus, the charcoals of these samples were almost completely composed of homocyclic aromatic C. Fig. 5 is a difference plot of the charcoal *versus* extractable organic matter of sample 22, clearly showing the enrichment of benzene and a series of PAHs in the charcoal, and a relative depletion of all other compounds (see also Appendix A). Many of the carbohydrate and N-compound markers present in the extractable fraction were absent in the charcoals studied.

The charcoal of sample three differed from the other charcoals analysed. It had a lower benzenes content (51%, of which 67% benzene), with 26% carbohydrates, 7.0% phenols, 6.7% lipids, 4.5% PAHs, 2.6% N-compounds and 2.1% lignins. The most striking feature of this charcoal was its enrichment in the carbohydrate marker levoglucosan (EF^2 = 7.8) and the lignin markers guaiacol, 4-vinylguaiacol and some compounds that were negligible in the pyrolysates of the extractable organic matter (levoglucosenone and methyl- and ethylguaiacol). Whereas the pyrolysis fingerprint of the carbohydrates

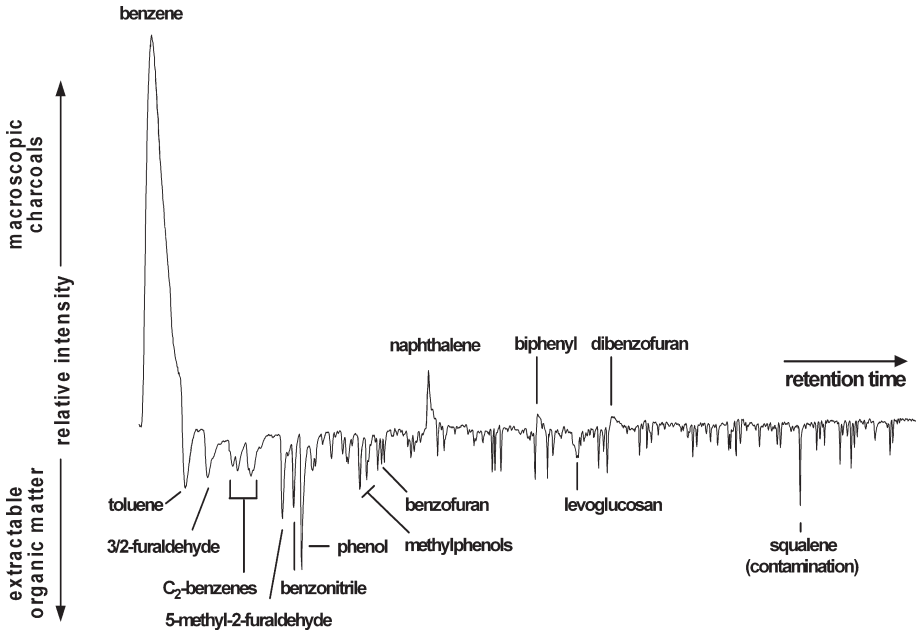

Fig. 5. Difference plot of sample 22: total ion current of the macroscopic charcoal minus the normalised TIC of the NaOH-extractable organic matter.

of the extractable organic matter was dominated by furans upon pyrolysis, the charcoal pyrolysate of sample three had a levoglucosan contribution of 16.2%, with 4.3% levoglucosenone, and minor amounts of furans. This implied that - besides enrichment in benzenes – lignins and intact polysaccharide pyrolysis products (levosugars) were relatively abundant in the charcoals of sample three. It is likely that the levosugars and lignin markers were derived from an intact lignocellulose (the major component of wood) core (cf. Knicker et al., 2005). These pyrolysis products were not found in the older charcoals because these were devoid of a core of unaltered biomass or such a core had already been decomposed. Thus, although charcoals are part of the BC continuum, they do not necessarily consist completely of BC (Forbes et al., 2006), and, paradoxically, the material least affected by fire is sometimes found within charcoal particles.

Burning of non-woody material rarely produces charcoal (Figueiral and Mosbrugger, 2000), and the charcoal and soot that is formed can be expected to have dimensions smaller than 2 mm. Therefore, the macroscopic charcoal record probably represents forest- or bushfires, while the pyrolysis signature of the extractable organic matter may include all forms of the BC continuum. The aromatic N-compounds are considered pyrolysis products of residues of burnt non-woody material as wood consists mainly of lignocellulose and is characterised by a high C/N ratio (Knicker et al., 2005). Indeed, the macroscopic charcoals had very small EFs for the N-compounds (Appendix A), except for benzonitrile, a potential pyrolysis-GC/MS indicator of BC (see above). The lack of N-containing pyrolysis markers in the charcoal and their abundance in the extractable pyrogenic C clearly indicates that molecular compositions of the various forms of BC can be very different. Essentially, the pyrolysis products of the extractable organic matter that were ascribed to BC were indeed concentrated in the charcoal fragments, accounting for 60–98% of total identified peak area. However, whether these pyrolysis products are indeed the principal pyrolysis products of BC requires more evidence from different soil types. The authors believe that that the results presented here, in combination with the predominance of aryl C resonances in NMR spectra (Kaal et al., 2008b), are strong evidence of a high BC concentration in the soil.

3.3. Acid colluvial soil (Atlantic ranker) in the light of fire

Pyrolysis-GC/MS suggested that the organic matter was mostly composed of degraded organic matter (carbohydrates and most N-compounds), lipids and BC. The lipids and degraded organic matter may have been chemically stabilised by bound poorly-crystalline Al hydroxides, as the mineralisation rate of organic matter diminishes upon adsorption of Al (Schwesig et al., 2003). Additionally, recent evidence suggests that occlusion of degraded organic matter in microaggregates provides physical protection for such chemically not particularly stable organics in acidic soils rich in reactive Al (Nierop et al., 2005; Buurman et al., 2007). The persistence of BC in the soils could be ascribed to its intrinsic recalcitrance perhaps combined with sorptive preservation (Fernández et al., 1997). None of the pyrolysis products was statistically related to the C or organically-bound Al content. This suggests that if sorptive preservation is partially responsible for degraded organic matter accumulation in the soil studied, this process is not compound specific and must act on BC as well. Czimczik and Masiello (2007) hypothesised that the long-term storage of BC in acidic soil is facilitated by interactions with a reactive soil matrix. This hypothesis is in accord with the results of the present study: a combination of chemical recalcitrance and sorptive protection by adsorbed Al hydroxides may have enabled BC storage in the soil. Recapitulating, the longevity of the organic matter can be explained by a combination of thermal modifications (charring), physical protection in microaggregates and non-selective adsorption of poorly-crystalline Al species. The relative importance of each stabilisation pathway is unknown. Nonetheless, if future studies point out that other acidic colluvial soils or Atlantic rankers contain large amounts of BC, charring may have to considered to be a significant force in the accumulation of organic matter.

4. Conclusions

- The extractable organic matter of an acidic colluvial soil (Atlantic ranker) from NW Spain that represents over 8.5 ka of colluviation showed clear evidence of burning throughout the profile. Thus, the area was subjected to recurrent fires and harbours significant amounts of BC.
- It appeared that fire remains yield benzenes, PAHs and benzonitrile, although many other pyrolysis products may originate from BC as well (such as N- and O-containing aromatic heterocyclics).
- Fire may at least be partially responsible for the long-term storage of C in the study area. The resistance of BC to biodegradation combined with the stabilising effect of adsorption to Al hydroxides could explain why large amounts of soil organic matter accumulated in the soil.

Acknowledgements

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Appendix A

Maximum, minimum and average contribution (in% of total identified peak area) of individual pyrolysis products to the NaOH-extractable organic matter and enrichment factors (EF, see text) for the charcoals.

Compound	*m*/*z*	Flag	Max [%]	Min [%]	Average [%]	EF chars 14,15, 19,22[a] [–]	EF char 3 [–]
Benzene	77 + 78	Benzene	16.8	3.91	11.4	6.03	3.09
Toluene	91 + 92	Benzene	19.6	7.04	14.3	0.46	0.80
Ethylbenzene	91 + 106	Benzene	1.48	0.75	1.15	0.13	0.61
1,2-Dimethylbenzene	91 + 106	Benzene	1.73	0.82	1.25	0.19	1.24
p-Xylene	91 + 106	Benzene	1.72	0.67	1.14	0.15	0.47
Styrene	78 + 104	Benzene	2.07	1.21	1.60	0.15	0.48
3/2-Furaldehyde	95 + 96	Carbohydrate	11.4	5.39	9.02	0.03	0.48
5-Methyl-2-furaldehyde	109 + 110	Carbohydrate	7.00	3.14	5.08	0.03	0.28
2-Methylfuran	53 + 82	Carbohydrate	2.93	1.65	2.33	–[b]	–[b]
2H-Furan-3-one	54 + 84	Carbohydrate	2.67	0.77	1.64	–[b]	–[b]
Acetic acid	60	Carbohydrate	5.61	1.65	3.95	–[b]	–[b]
Levoglucosan	60 + 73	Carbohydrate	2.49	0.00	1.31	0.54	7.83
Naphthalene	128	PAH	3.52	0.50	1.66	1.68	1.09
Benzofuran	89 + 118	PAH	1.36	0.61	1.04	0.53	1.01
½-Methylnaphthalene	141 + 142	PAH	1.81	0.60	1.00	0.25	0.82
Biphenyl	153 + 154	PAH	1.10	0.25	0.61	0.70	0.48
Fluorene	165 + 166	PAH	1.38	0.19	0.54	0.54	0.59
Dibenzofuran	139 + 168	PAH	1.50	0.43	0.78	1.10	0.77
Anthracene/phenanthrene	178 + 176	PAH	0.93	0.28	0.47	0.69	0.92
Pyrene (fluoranthene?)	202	PAH	0.38	0.07	0.16	–[b]	–[b]
Pyrrole	67	N-Compound	4.43	0.90	1.77	–[b]	–[b]
3-Methylpyrrole	80 + 81	N-Compound	3.76	0.59	1.18	0.06	0.28
Diketodipyrrole	93 + 186	N-Compound	0.55	0.17	0.35	–[b]	0.44
Pyridine	52 + 79	N-Compound	7.95	3.49	5.25	0.02	0.08
2-Methylpyridine	66 + 93	N-Compound	1.18	0.47	0.71	–[b]	–[b]
3-Methylpyridine	66 + 93	N-Compound	2.01	0.92	1.22	–[b]	–[b]
Indole	90 + 117	N-Compound	0.76	0.23	0.40	–[b]	–[b]
Benzonitrile	76 + 103	N-Compound	5.54	2.02	3.41	0.44	0.51
(Iso)quinoline	102 + 129	N-Compound	0.22	0.09	0.14	–[b]	–[b]
Phenol	66 + 94	Phenol	11.1	7.07	9.28	0.13	0.38
2-Methylphenol	107 + 108	Phenol	1.50	0.48	0.75	0.04	0.78
4-Methylphenol	107 + 108	Phenol	2.49	1.18	1.65	0.05	0.93
Guaiacol	109 + 124	Lignin	0.79	0.00	0.21	0.03	3.17
4-Vinylguaiacol	135 + 150	Lignin	0.33	0.00	0.09	0.57	3.00
C_3–C_{10}-Alkylbenzene	91 + 92	Lipid	0.39	0.11	0.23	0.25	0.50
C_{11}–C_{15}-Alkylbenzene	91 + 92	Lipid	0.20	0.02	0.07	0.27	0.94
C_{16}–C_{20}-Alkylbenzene	91 + 92	Lipid	0.12	0.01	0.04	0.46	1.49
C_3-Naphthalene	155 + 170	Lipid	0.82	0.07	0.27	–[b]	–[b]
C_{10}–C_{15}-Alkane	57 + 71	Lipid	0.93	0.11	0.30	0.25	0.86
C_{16}–C_{20}-Alkane	57 + 71	Lipid	1.17	0.08	0.30	0.22	0.73
C_{21}–C_{25}-Alkane	57 + 71	Lipid	0.91	0.12	0.31	0.50	1.10
C_{26}–C_{30}-Alkane	57 + 71	Lipid	0.58	0.10	0.24	0.99	1.47
C_{31}-Alkane	57 + 71	Lipid	0.38	0.07	0.21	0.41	1.00
C_{33}-Alkane	57 + 71	Lipid	0.39	0.04	0.13	0.64	1.13
C_{11}–C_{15}-Alkene	55 + 69	Lipid	1.02	0.14	0.37	0.28	1.08
C_{16}–C_{20}-Alkene	55 + 69	Lipid	0.82	0.06	0.21	0.20	0.77
C_{21}-C_{25}-Alkene	55 + 69	Lipid	0.61	0.06	0.18	0.29	0.94
C_{26}–C_{28}-Alkene	55 + 69	Lipid	0.31	0.04	0.11	0.60	1.04

[a] Average of four samples.
[b] EF = 0 (compound not found in charcoal pyrolysates).

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Holocene fire history of black colluvial soils revealed by pyrolysis-GC/MS: a case study from Campo Lameiro (NW Spain)

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Abstract

The colluvial soils of Galicia (NW Spain) are records of Holocene environmental change. In spite of the omnipresence of charcoal fragments in these soils, the effect of fires on the development of the Galician landscape and the potential role of past societies are poorly understood.

We isolated macroscopic charcoal (>2 mm) and NaOH-extractable soil organic matter (SOM) from two Galician soils. Molecular characterisation of the extractable SOM using pyrolysis-GC/MS showed that fire residues (black carbon; BC) were abundant in the extractable SOM, even in the horizons containing few macroscopic charcoals. This indicates that the macroscopic charcoal record often used in geoarchaeological studies gives an incomplete image of the fire history.

Polycyclic aromatic hydrocarbons and other presumably BC-derived pyrolysis products in samples from 8500 to 7000 cal years BP are evidence of Mesolithic fires. Molecular indicators of BC are abundant also in the Neolithic (*c*. 6000 BP), but the degree of thermal modification to the organic matter decreases, which could mirror a change in fuel type. This change coincides with the beginning of accelerated soil erosion in the area, and is followed by accumulation of relatively homogeneous BC-rich material up to at least the beginning of the Iron Age. This pattern is interpreted as deforestation around 6000 BP followed by periodic and presumably human-induced burning of poorly-developed vegetation (slash-and-burn). The open landscape of present-day Galicia would therefore be the outcome of prolonged anthropogenic burning, analogous to the open cultural landscapes of central Europe.

Keywords: Fire history; Black carbon; Colluvial soil; Galicia; Pyrolysis-GC/MS

1. Introduction

The area of Campo Lameiro is one of the largest concentrations of rock art in Galicia (NW Spain; Fig. 1). Iconographic studies indicated that these rock carvings were created between 4500 and 2500 cal BP (Santos Estévez, 2005). A geomorphological survey showed that the rock art panels were exposed since the Bronze Age (4500–3000 BP), which is the onset of potential rock carving (Costa Casais et al., in press). More precise information of petroglyph creation and the societies responsible for them is thus far unavailable due to the lack of archaeological remains collected from excavations in the area. Nonetheless, it is aimed to convert the ''Rock Art Park of Campo Lameiro'' into a major tourist attraction by the construction of a museum.

The investigation of soil properties could give further information when archaeological artefacts are missing. Galicia harbours a soil type that is traditionally referred to as 'Atlantic ranker' (Carballas et al., 1967; Duchaufour, 1982), but

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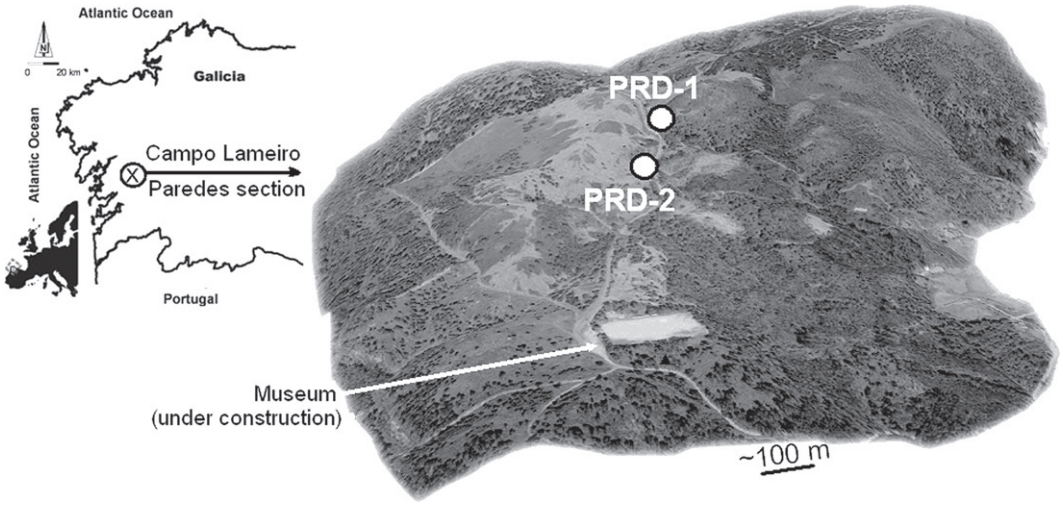

Fig. 1. Study area.

nowadays terms like aluandic acid soil, umbric soil and aluminic soil are preferred (Macías et al., 1982; García-Rodeja et al., 2004). Being the result of thousands of years of erosion and sedimentation processes (colluviation), Atlantic rankers consist of a sequence of A-horizons that often carry evidence of intensified erosion (gravel and stone layers) and fire episodes (charcoals). These soils are natural archives that can be used to reconstruct the human impact on the landscape/environment (Kalis et al., 2003).

Previous work suggested that fire may have been an important factor in the formation of the soils of Campo Lameiro (Kaal et al., 2008). Incomplete combustion of biomass produces a diverse set of residues that is collectively referred to as black carbon (BC). Black C types, ranging from slightly charred organic matter to soot, have in common that they are highly aromatic and relatively resistant against biodegradation (Forbes et al., 2006). The latter property gives BC a potential role in the global C cycle as a sink for atmospheric CO_2 (Seiler and Crutzen, 1980; Goldberg, 1985; Kuhlbusch and Crutzen, 1995) rendering BC a popular subject (reviews: Schmidt and Noack, 2000; González-Pérez et al., 2004; Preston and Schmidt, 2006).

Apart from its potential function as a climate mediator, fire has been and still is a factor in the development of landscapes. The present-day open cultural landscape of central Europe is the result of human intervention since at least 6000 cal BP (Early Neolithic), very likely in the form of the deliberate use of fire (Carcaillet et al., 2002). Because vegetation fires and human land-use are often closely interconnected, macroscopic charcoal records together with pollen and other macrofossils are used to reconstruct the fire history and human interference in the environment (e.g. Carcaillet, 1998; Figueiral and Mosbrugger, 2000).

In Atlantic rankers, changes in the vegetation community and in the degradation processes of its dead remains are reflected by changes in the depth/age profile of the organic matter composition. Fire-induced thermal modifications to plant material previous to incorporation in the soil can be recognised by characterisation of the organic matter. The advantage of molecular characterisation over macroscopic charcoal separation is that disintegrated and partially degraded or humified BC, or fine-grained BC produced upon the burning of non-woody vegetation, can be detected while escaping the analytical window of macroscopic charcoal analysis (Figueiral and Mosbrugger, 2000).

In this paper we discuss the chemical fingerprint of soil organic matter (SOM) as obtained using pyrolysis-gas chromatography/mass spectrometry (pyrolysis-GC/MS). The principal objective is to relate the organic matter composition to the fire history of the Campo Lameiro area and discuss the likelihood of human intervention.

2. Methods and materials

2.1. Study site

The study area (*Paredes* (PRD), Campo Lameiro, NW Spain) is an isolated hill located at 25 km from the Atlantic coast (Fig. 1). The local bedrock is a migmatitic granite. The soils analysed are black, sandy, acidic, organic-rich colluvial soils, formed by multiple erosion and sedimentation phases during the Late Pleistocene and the Holocene.

Representations of the soil profiles are given in Fig. 2. Soil PRD-1 is a 1.5 m thick colluvium that formed discontinuously from the Late Pleistocene onwards (Costa Casais et al., in press). Soil PRD-2, located at 150 m downslope from PRD-1, is 2.4 m thick but represents only 6000 years of accumulation. Samples were taken from soil monoliths at regular intervals of 5 cm until the base of the profile. Macroscopic charcoals (>2 mm) were collected by wet sieving.

2.2. Dating of samples

Before radiocarbon analysis soil samples (fine earth fraction, <2 mm) were shaken in ultrapure distilled water for 16 h, and then the suspension was filtrated on a 50 μm

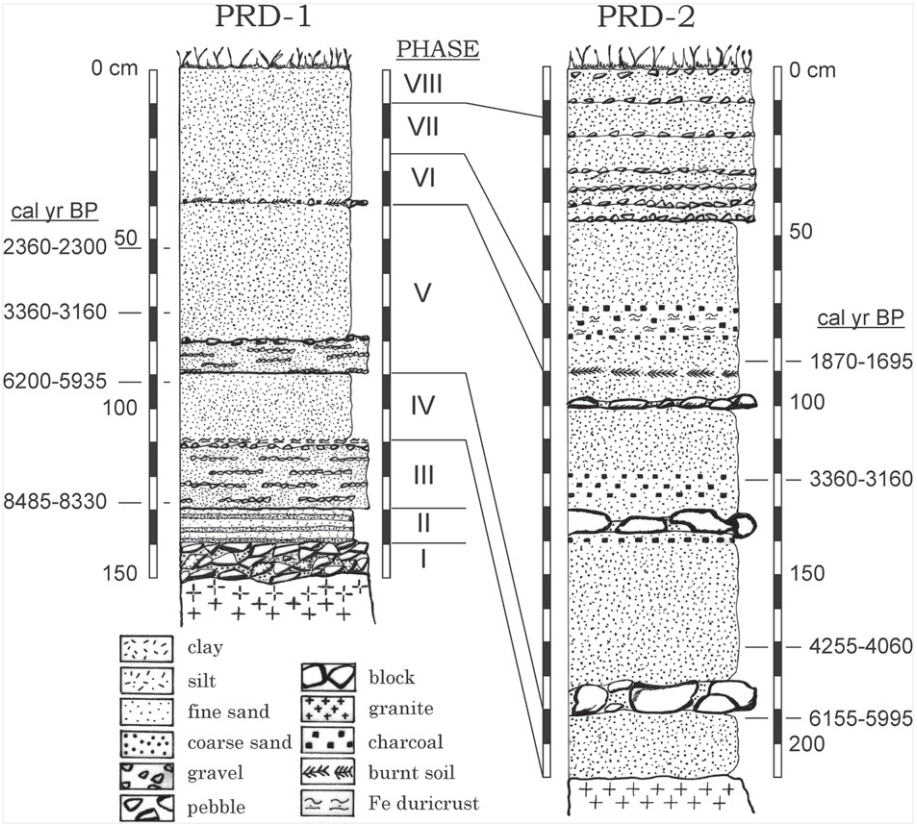

Fig. 2. Profiles and radiocarbon ages (in 2σ cal years BP) of PRD-1 and PRD-2. Roman numbers refer to the phases that are described in Section 3.3.

mesh-size sieve, thereby removing sand, roots and some undecomposed organic remains. Radiocarbon age determinations were performed on 'humic acids' obtained by the standard acid-alkaline-acid isolation procedure of The Ångstrom Laboratory (Uppsala, Sweden): (1) removal of carbonates by 1% HCl; (2) isolation of the organic matter soluble in 1% NaOH solution held just below boiling point for 8–10 h; and (3) subsequent precipitation of the soluble fraction in concentrated HCl. Next, the washed and dried organic material was converted to graphite using a Fe-catalysed reaction. Accelerator mass spectrometry (AMS) was performed at the radiocarbon facility of The Ångstrom Laboratory. ^{14}C concentrations were calibrated using CALIB 5.0.1 (Stuiver and Reimer, 1993). Results are given in Fig. 2 as 2σ cal years BP. Age estimations of other samples were based on synchronicity of charcoal or stone layers, while samples with no such reference were assigned by linear intrapolation between dated samples. In this paper, ages that refer to dated samples are given as 2σ cal years BP (cal BP), while calculated age estimations are reported as *c*. years BP. Carbon and macroscopic charcoal content are plotted against the measured or estimated age in Fig. 3 to support the fire history reconstruction (Section 3.3).

2.3. Soil organic matter (SOM) extraction and purification

For organic matter characterisation, SOM was separated from the fine earth fraction by extraction with 0.1 M NaOH (10 g soil:50 ml aqueous NaOH) (twice) and water (3–5 times, until the supernatant was colourless). Decanting of extracts was always preceded by centrifugation at $\sim 1000 \times g$ for 15 min. The extracts were combined and acidified to pH 1.5–2.0 with 4:1 HF/HCl solution. Fine roots and smaller charcoals (63 μm–2 mm) were removed from the extracts with a 63 μm mesh-size sieve and discarded. Extracts were subsequently dialysed against distilled water and freeze-dried. Extraction yields for C, calculated from elemental analysis of the residues and the untreated fine earth fraction, were $82 \pm 12\%$ and $82 \pm 9\%$ for PRD-1 and PRD-2, respectively. Only a small fraction of inextricable C was accounted for by the fine roots and smaller charcoals.

2.4. Pyrolysis-GC/MS

Curie-point pyrolysis-GC/MS was performed on 28 samples of extracted SOM from PRD-1, of which two were analysed in duplicate, and 16 samples from PRD-2 (one analysed in triplicate) on a pyrolyser from Horizon Instruments. The Curie temperature of the ferromagnetic wire was 600 °C. Pyrolysis products were transported to the GC (Carlo Erba GC 8000) under a flow of He. The GC was equipped with a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51b (film thickness 0.40 μm). The initial oven temperature was 40 °C and the heating rate 7 °C min^{-1}. The final temperature of 320 °C was maintained for 20 min. The GC column was coupled to a Fisons MD 800 mass

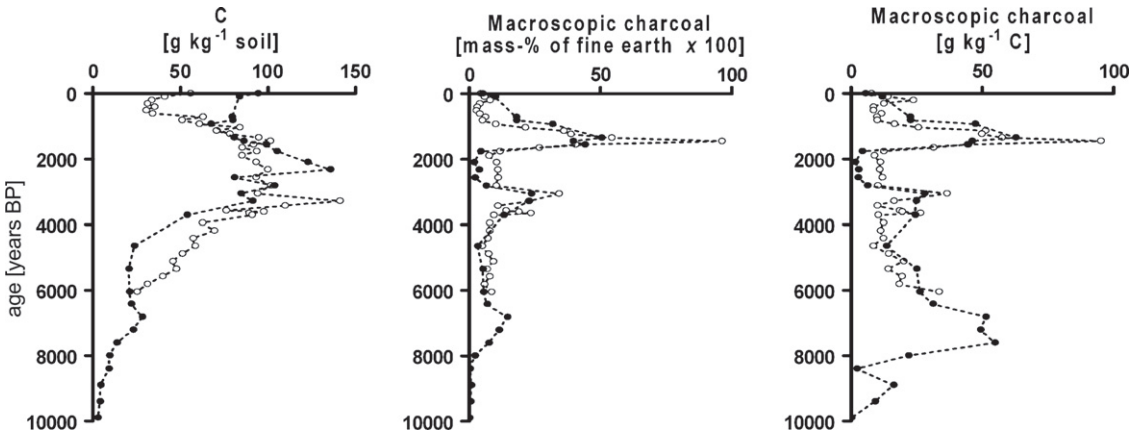

Fig. 3. Carbon and macroscopic charcoal content, and the amount of macroscopic charcoal per C unit, plotted against estimated age. ●: PRD-1, ○: PRD-2.

spectrometer (mass range *m*/*z* 45–650, cycle time 1 s) operating at an electron impact energy of 70 eV. All major peaks in the chromatogram were used for quantification, generally by measuring the combined peak area of the two principal fragment ions of a pyrolysis product. Additional signals of less abundant compounds such as the alkane/alkene doublets that originate from lipids lead to a total number of 94 quantified pyrolysis products. All peaks had to be checked manually due to differences in retention times and sometimes incorrect baseline estimations by the software. Although each pyrolysis product has a different relative response factor and therefore peak areas cannot be translated to absolute concentrations, we make the assumption that the response factor of each product is unity. The results are therefore only semi-quantitative, but this does not inhibit reliable comparison between samples. The probability that the SOM contained significant amounts of BC was discussed in Kaal et al. (2008) using the ^{13}C NMR (nuclear magnetic resonance) and pyrolysis-GC/MS data of soil PRD-1.

3. Results and discussion

3.1. Assumptions

In the following section we assume that: (1) ^{14}C ages correspond to the age of deposition (see below); (2) the SOM is immobile since burial (Kaal et al., in press); (3) the composition of extractable SOM determined by pyrolysis-GC/MS is representative of the organic matter present in the soil material, although not all SOM was extractable and pyrolysis-GC/MS is a semi-quantitative method; (4) macroscopic charcoals are products of local burning of woody plant material (Patterson et al., 1987); and (5) that a peak in macroscopic charcoal content implies a synchronous maximum in its formation, i.e. that *variations* in the fraction of charcoal removed by wind and water erosion did not exert significant influence on the amount of charcoal measured.

The first assumption is crucial in this study and requires further explanation. Soil organic matter is a complex mixture of organic compounds in different degradation states and different ages. While charcoal is relatively insensitive to biological decay processes and incorporation of juvenile organic matter, and therefore suitable for ^{14}C measurements (Scharpenseel and Becker-Heidmann, 1992), in most systems bulk soil organic matter is not (Kristiansen et al., 2003). This is primarily due to incorporation of juvenile organic matter in buried soil layers, (Scharpenseel and Becker-Heidmann, 1992). Such 'rejuvenation' occurs through bioturbation or leaching of fresh organic matter, and an input of organic matter from roots into buried horizons (Orlova and Panychev, 1993; Nierop et al., 1999). When rejuvenation is significant, measured ^{14}C ages are younger than the depositional age (Wang et al., 1996).

The measured ^{14}C age of the organic matter in the soils studied is thought to be representative – within the uncertainty of age calibration – of the period in which the source vegetation died and the organic remains were incorporated into the soil, because of the following characteristics of the organic matter used for ^{14}C measurements and soil properties: firstly, radiocarbon dating was performed on humic acids lacking fresh organic matter (Pessenda et al., 2001; Kovda et al., 2001). In Atlantic rankers, humic acids account for the vast majority of soil carbon (Carballas et al., 1967). Mobilisation of the 'humified' organic matter in these soils is inhibited because of the abundance of reactive Al-hydroxides that bind to it (Carballas Fernández, 1982; Kaal et al., in press). The proportion of fresh organic matter is small not only because of the pre-treatment employed, but also because pyrolysis-GC/MS showed that very few remains of intact lignin and polysaccharide are present in the NaOH-extractable fraction (this paper). Consequently, it is very unlikely that the postburial incorporation of juvenile organic matter significantly affected the ^{14}C measurements of the dated fraction. Secondly, eight samples from three other soil profiles from Campo Lameiro provided radiocarbon ages that are in agreement with the stratigraphical sequences of the soils discussed here. Thirdly, extracted SOM and charcoal samples obtained from the same layers of an Atlantic ranker located at 40 km from Campo Lameiro gave indistinguishable ^{14}C ages (Martínez Cortizas et al., 2000). Finally, records of forest clearances, soil erosion/sedimentation phases and atmospheric metal pollution in NW Spain reconstructed using peat records showed synchronicity with the

same processes detected in soils and reconstructed based on datings of SOM (Fábregas Valcarce et al., 2003; Martínez Cortizas et al., 2005). As peat ^{14}C datings are widely accepted as genuine indications of the death of the vegetation from which the C originates, the compatibility of peat records with those of Atlantic rankers indicates these acid, organic matter rich, colluvial soils can be used as archives as well – although with a lower time resolution. The age/depth relation of soil and peat stratigraphy was also shown to be consistent from peat and Andosol humic acids from Ecuador (Tonneijck et al., 2006). One uncertainty remains, however, and that is the potential redistribution of old soil material on top of younger surfaces, producing an age inversion in the depth profile of the soil (Lang and Hönscheidt, 1999). Therefore, ^{14}C ages are indicative of when the organic matter first entered the erosion-transportation-deposition pathway, not necessarily of the age of burial. The soils studied here were characterised by a wide array of different methods operating at different soil fractions, and none of these indicated such inversions occurred, which is why we believe it is legitimate to use the ^{14}C ages as approximations of the time of deposition.

3.2. Organic matter composition

Table 1 is a list of pyrolysis products with their average contributions to the two profiles studied. The differences in average SOM composition between the profiles are very small. The pyrolysates were dominated by benzenes (predominantly benzene and toluene), furans, benzonitrile, heterocyclic N-containing compounds, polycyclic aromatic hydrocarbons (PAHs), lipids and phenols. Summation of pyrolysis products within each class gives concentration profiles of component classes (Fig. 4).

BENZENES – Benzenes have an unusually large contribution to the chromatograms (up to 45% of total quantified peak area). Although these benzenes may form upon pyrolysis of various aromatic biocomponents, e.g. lignin and tannin, their large contribution suggests that they derive from BC, because organic matter is transformed into aromatic structures during thermal alteration (Naafs, 2004) and because these alternative sources additionally produce methoxyphenols or catechols upon pyrolysis, which were negligible. Recent methodological studies showed that BC can be effectively characterised and distinguished from non-BC organic matter using pyrolysis-GC/MS, and that benzene and toluene are indeed the principal pyrolysis products of BC (de la Rosa Arranz, 2007). In PRD-1, the contribution of benzenes after pyrolysis fluctuates slightly around 30% from the surface down to 1.10 m depth (*c*. 7000 BP), where it reaches an abrupt maximum of 45%. For PRD-2, benzenes contribution is also between 25 and 35%, except for the soil layer that corresponds to the youngest macroscopic charcoal peak, in which the benzene contribution reaches almost 45%.

CARBOHYDRATES – The carbohydrate fraction produces primarily furans (including furaldehydes) and acetic acid upon pyrolysis. Although these carbohydrate markers can be generated upon pyrolysis of the polysaccharide cellulose, the small contribution of cellulose's principal pyrolysis product, i.e. levoglucosan, is indicative of the degraded state of the carbohydrates (Poirier et al., 2005). The furans are likely to have derived from degraded and microbial (hereafter degraded) carbohydrates, although a pyrogenic fraction cannot be ruled out (Pastorova et al., 1994). In the following discussion on the fire history of the area (Section 3.3), the furans are considered biodegradation products.

Levoglucosan is concentrated at the surface and diminishes with depth (not shown), while the other carbohydrate markers, except for 2H-furan-3-one in PRD-2, do not exhibit a significant depth trend. Consequently, the sum of carbohydrate markers remains constant at ca. 20–25%, which is indicative of a stabilisation mechanism of degraded or BC-derived carbohydrates. Stabilisation of degraded carbohydrates over large time scales is a characteristic of some soils having andic properties (Nierop et al., 2005; Buurman et al., in press), of which the cause is still unknown.

LIGNINS – Lignin markers are scarce (<1.5%). The lignin markers represent the pyrolysis products of biologically "intermediate labile/stable" (in contrast to "stable", i.e. the lipids) forms of mainly primary organic matter. In both soils, the contribution of lignin markers declines exponentially from 1 to 1.5% at the surface towards 0.2% at *c*. 6000 BP, after which disappearing in PRD-1. The scarcity of lignin is the combined effect of charring, which removes their characteristic methoxyl functionality (Knicker et al., 2005) and probably biodegradation.

PROTEINS – N-containing pyrolysis-products (Table 1) ultimately derive from protein structures. Nonetheless, their origin is distinct. Pyrolysis product (iso)quinoline (i.e. naphthalene with one C atom replaced by N) and benzonitrile are possible fire products (Alcañiz et al., 1994). Benzonitrile is indeed abundant (up to 6.9%). Pyrroles, pyridines and indole can derive from primary proteinaceous structures (Schulten and Schnitzer, 1998) and their degradation products. Pyridine shows a maximum in charcoal-rich horizons and could therefore additionally originate from BC, and pyrroles can also partly originate from BC (González-Pérez et al., 2004). The large contribution of N-containing pyrolysis products (10–20%) suggests a degraded state of the proteins by itself, because intact proteins split into small and volatile moieties of which the N-carriers are poorly observed in pyrolysates of complex mixtures (Chiavari and Galletti, 1992).

PHENOLS – Phenols derive from e.g. lignin, tannin, proteins and polysaccharides. Phenols account for 7–15% of the pyrolysate. The phenols contribution is relatively constant, although the youngest charcoal peak coincides with a minimum in phenols in PRD-2, suggesting the dehydroxylation or destruction of the majority of the parent substances of phenols during that particular fire event.

PAHS – The contribution of PAHs ranges from 3 to 12%. This sum does not include cyclisation products of lipids (C_3–C_{20} alkylbenzenes and propylnaphthalene; Saiz-Jiménez, 1994; Kaal et al., 2008). The PAHs labeled as such are evidence of the presence of BC-derived material in the SOM fraction (Naafs, 2004; de la Rosa Arranz, 2007). PAHs are

Table 1
Summarised results of pyrolysis-GC/MS: component classes (in capitals), compounds list, assumed principal source of pyrolysis products and average contributions of component classes and individual products to total quantified peak area

Class	Compound	Principal source	PRD-1 ($n = 30$)		PRD-2 ($n = 18$)	
			Average [%]	SD[a]	Average [%]	SD[a]
BENZENES			31.3	5.0	33.7	5.5
	Benzene	BC	11.6	2.7	13.8	4.9
	Toluene	BC	14.5	2.4	15.1	1.3
	Ethylbenzene	Unspecific	1.2	0.2	0.9	0.3
	1,2/3-dimethylbenzene	Unspecific	1.3	0.2	1.3	0.3
	p-xylene	Unspecific	1.1	0.2	1.1	0.3
	Styrene	Unspecific	1.6	0.2	1.6	0.1
CARBOHYDRATES			23.3	3.7	23.0	4.2
	2/3-furaldehyde	Degraded SOM/BC	8.9	1.6	8.1	1.8
	5-methyl-2-furaldehyde	Degraded SOM/BC	5.1	0.9	4.5	0.8
	acetic acid	Unspecific	3.9	1.2	4.6	1.4
	2-methylfuran	Degraded SOM/BC	2.3	0.3	2.3	0.2
	2H-furan-3-one	Degraded SOM/BC	1.6	0.4	1.6	0.7
	Levoglucosan	Primary SOM	1.4	0.5	2.1	1.1
N-COMPOUNDS (PROTEINS)			14.2	2.3	14.6	1.7
	Pyridine	Degraded SOM/BC	5.2	1.2	5.3	1.0
	Benzonitrile	BC	3.5	0.9	4.1	1.5
	Pyrrole	Degraded SOM	1.7	0.6	1.6	0.6
	3-methylpyridine	Degraded SOM/BC	1.2	0.2	1.2	0.2
	2-methylpyridine	Degraded SOM/BC	0.7	0.1	0.7	0.1
	3-methyl-1H-pyrrole	Degraded SOM	1.1	0.6	1.1	0.2
	Indole	Degraded/primary SOM	0.4	0.1	0.4	0.1
	Diketodipyrrole	Degraded/primary SOM	0.3	0.1	0.3	0.1
	(Iso)quinoline	BC	0.1	0.0	0.0	0.0
LIPIDS		Primary SOM	12.8	6.0	10.1	2.3
PHENOLS			11.7	1.3	12.5	2.6
	Phenol	Unspecific	9.3	1.1	10.0	2.0
	4-methylphenol	Unspecific	1.7	0.4	1.8	0.7
	2-methylphenol	Unspecific	0.7	0.2	0.7	0.2
PAHs			6.3	1.8	5.5	0.8
	Naphthalene	BC	1.7	0.6	1.5	0.3
	Benzofuran	BC	1.1	0.2	1.2	0.2
	Methylnaphthalene	BC	1.0	0.3	0.9	0.2
	Dibenzofuran	BC	0.8	0.3	0.7	0.2
	Biphenyl	BC	0.6	0.2	0.6	0.1
	Anthracene	BC	0.5	0.2	0.3	0.1
	Fluorene	BC	0.5	0.3	0.4	0.1
	Pyrene/fluoranthene	BC	0.2	0.1	0.1	0.0
LIGNINS			0.3	0.3	0.4	0.3
	Guaiacol	Primary SOM	0.2	0.2	0.3	0.2
	4-vinylguaiacol	Primary SOM	0.1	0.1	0.1	0.1

BC, black carbon; SOM, soil organic matter; PAHs, polycyclic aromatic hydrocarbons.
[a] Standard deviation.

relatively constant up to *c*. 6000 BP, and show large fluctuations in the samples of PRD-1 older than that. The lowest value is obtained for the sample at the bottom of that profile. The inverse relation between carbohydrates and PAHs suggests that PAHs originate from carbohydrate-derived BC (Boon et al., 1994; Pastorova et al., 1994).

LIPIDS – The lipids are predominantly alkane/alkene doublets. Fatty acids gave small and broad unquantifiable peaks. Preliminary experiments using Thermally assisted Hydrolysis and Methylation (THM) showed that the lipids are almost completely plant-derived (not shown). Whether the increase with depth of lipids is caused by selective preservation (Baldock et al., 1992, and references cited therein) or gradual neoformation of aliphatic geopolymers (de Leeuw et al., 2006), the alkane/alkene doublets observed with pyrolysis-GC/MS are not biodegradation products and therefore labeled ''primary'' in Table 1.

The last graph in Fig. 4 shows the sum of the pyrolysis products that have an almost certain BC origin: benzene, PAHs, benzonitrile and isoquinoline. This sum is lowest at the bottom of profile PRD-1, then increases towards 30–35% around 8000 BP, after which it remains an approximate 25–30% in both soils, except for a maximum during the youngest macroscopic charcoal peak *c*. 1500 BP.

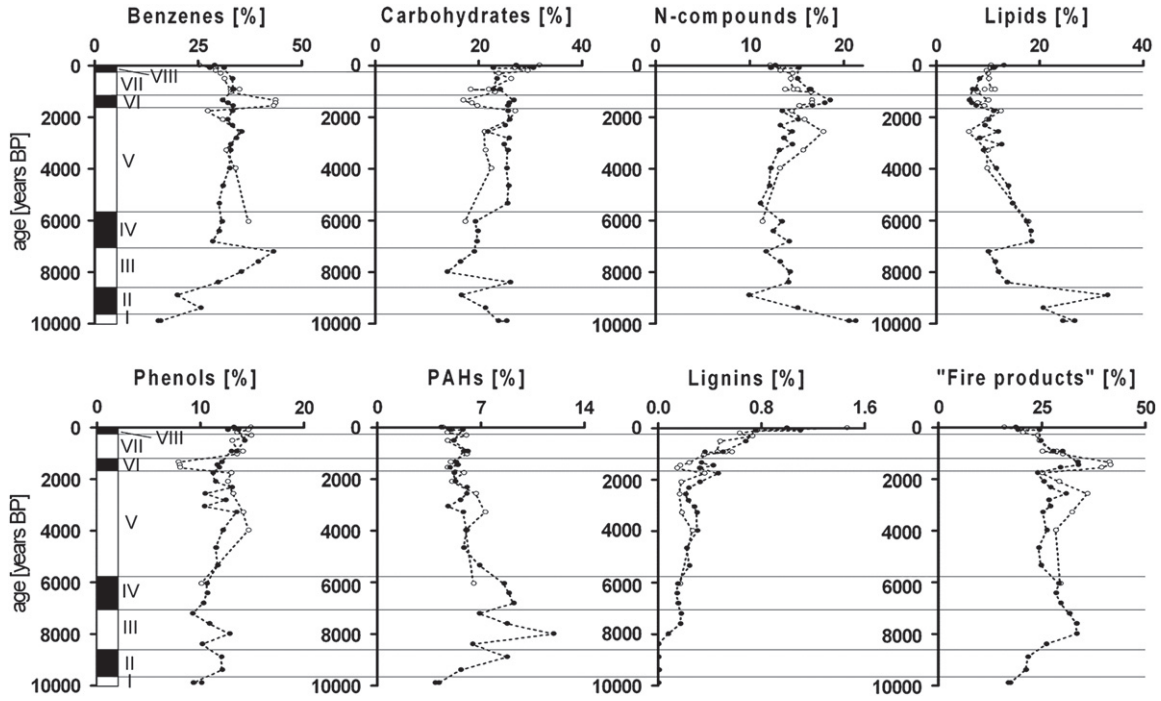

Fig. 4. Component class proportions (in % of total quantified peak area) obtained by pyrolysis-GC/MS plotted against estimated age. "Fire products" is the joint contribution of benzene, PAHs, benzonitrile and (iso)quinoline. Roman numbers refer to the phases in Fig. 2 that are described in Section 3.3. ●: PRD-1, ○: PRD-2.

In brief, the SOM yields a complex mixture of the likely products of labile and intermediate labile/stable primary (lignin markers and levoglucosan), stable primary (lipid markers), degraded (furans, pyrroles, pyridines, etc.) and presumably BC-derived organic matter (benzenes, PAHs, benzonitrile, isoquinoline and some pyridine) upon pyrolysis. The following discussion on the fire history builds on variations of the relative abundances of these organic matter forms within and between soil profiles.

3.3. Fire history

Horizonation and pyrolysis-GC/MS fingerprints of the SOM allows us to identify phases in the evolution of the soils (Figs. 2 and 4). The three phases before ca. 6300 BP in PRD-1 do not have a chronological analogue in PRD-2.

PHASE I – Phase I is represented by the bottom sample of PRD-1 consisting of strongly weathered transported saprolite which was deposited before 8485–8330 cal BP, and possibly dates from the Younger Dryas (12,900–11,500 cal BP; Costa Casais et al., in press). Its SOM produces an above average amount of lipid markers, carbohydrates and N-containing compounds upon pyrolysis. The carbohydrate markers and N-containing pyrolysis products that are concentrated in Phase I are indicators of degraded SOM (e.g. the furans and pyrroles). The BC-derived pyrolysis products are relatively unimportant (Fig. 4). Levoglucosan and guaiacols are below the quantitation limit. The SOM of Phase I constitutes a mixture of lipids and the products of carbohydrate and protein degradation. Fire was not a major factor in the formation of the SOM, which is supported by the absence of macroscopic charcoal (Fig. 3). If Phase I indeed derived from a pre-Holocene cold phase, the SOM probably derives from grasses and heliophilous plants growing in an open landscape (Santos et al., 2000).

PHASE II – Covering the section between 1.40 and 1.30 m depth of PRD-1, Phase II was also deposited before 8485–8330 cal BP, and is a fine-grained colluviated saprolite. Analogous to Phase I, Phase II is relatively enriched in lipids and devoid of markers of intact polysaccharide and lignin. The SOM of Phase II however does not yield as much degraded organic matter markers upon pyrolysis as does that of Phase I, and has a slightly higher level of BC-derived pyrolysis products. The SOM of Phase II is a mixture of primary stable (lipids), degraded and probably some BC-derived organic matter, the former being dominant. The few macroscopic charcoal fragments obtained support a small contribution of BC-derived SOM. Thus, assuming that the SOM and charcoal from these samples were incorporated in the soil before *c*. 8500 BP as suggested by radiocarbon dating, fire occurred already during the Early/Mid Mesolithic.

PHASE III – Starting with the sample dated 8485–8330 cal BP, Phase III is represented by the material between 1.30 and 1.10 m depth of PRD-1, deposited in the Mid Mesolithic. This layer contains various gravel-rich layers (Fig. 2), reflecting intense erosion episodes. After pyrolysis, its SOM exhibits increasingly high amounts of benzene towards the top of the phase, reaching 45% at 1.10 m, and is also enriched in PAHs (reaching a maximum exceeding 12%), albeit with a different concentration profile. The sum of "fire products"

(Fig. 4) contributes an estimated 30% of the pyrolysate, which is a conservative estimate of BC-derived pyrolysis products to the extractable and pyrolysable SOM, as other compounds-like toluene and pyridine- are probably pyrolysis products of BC as well. Besides the pyrolysis products of BC, significant amounts of pyrroles, furans, phenols and lipids are present, representing a mixture of primary and degraded SOM. In the BC-dominated SOM of Phase III, the contribution of lipids is relatively small. The presence of BC-derived SOM is corroborated by the coinciding peak in macroscopic charcoal content (Fig. 3). Although these charcoal fragments account for less than 5% of the organic matter in the soil (estimated from the ratio of macroscopic charcoal to total C; Fig. 3), a much larger amount of BC must be present as NaOH-extractable BC in the SOM fraction to account for the contribution of BC markers observed by pyrolysis-GC/MS. This may suggest degradation of charcoal-BC over large time scales and interference of BC in humic substances (Haumaier and Zech, 1995; Cohen-Ofri et al., 2006), perhaps combined with the input of the burning residues of non-woody vegetation. Moreover, extractable SOM can apparently contain more BC than the macroscopic charcoals, suggesting that macroscopic charcoal records provide an incomplete picture of the fire history.

Phase III reflects a series of fires that occurred roughly between 8500 and 7000 BP. The large contribution of organic matter producing PAHs upon pyrolysis is indicative of a highly condensed state of the aromatics, and therefore arguably of a relatively high intensity of the fire(s) which may suggest the burning of forest. Phase III coincides with forest fire records in northwest Spain around 7500–7000 BP (Martínez Cortizas, 2000). These results agree with the ubiquitous presence of charcoals in the soils from mid-altitude slopes of the Alps (Carcaillet et al., 2002). The nature of the Mesolithic fire regime (natural *vs.* anthropogenic) in many parts of Europe is still equivocal. Phase III ends at 1.10 m depth with an orange iron-rich layer in PRD-1 that is interpreted as burnt soil, which coincides with the onset of sediment accumulation at PRD-2.

PHASE IV – Phase IV covers the samples between 0.90 and 1.10 m in PRD-1 and 1.90 and 2.10 m in PRD-2. The upper samples of Phase IV were dated 6200–5935 cal BP (PRD-1) and 6155–5995 cal BP (PRD-2). From the relatively homogeneous nature of the soil material it is concluded that Phase IV is a period between *c*. 7000 and 6000 BP (the Early Neolithic) without intense erosion episodes. The lipid contribution of the SOM increases towards 20%, while the contribution of benzenes declines, which is indicative of a small BC contribution in comparison with the SOM of Phase III. PAHs levels remain high in PRD-1 and some charcoal is present, which supports the occurrence of fire. The SOM of Phase IV is mostly derived from BC and lipids, while the contribution of degraded organic matter is relatively small.

PHASE V – The boundary between phases IV and V reflects an erosion episode that occurred around 6000 BP. The deposit on top of this gravel/stone layer reflects a period of ca. 4000 years of sedimentation between *c*. 6000 and 2000 BP (covering the Neolithic, Bronze Age and Early Iron Age). This phase corresponds to 0.5 m of relatively homogeneous material in PRD-1 and a 1 m thick layer interrupted by charcoal accumulations and a stone layer (*c*. 3500–3000 BP) in PRD-2. This is indicative of the higher sediment accumulation rate at PRD-2. It is likely that Phase V includes various episodes of environmental change, not seen in PRD-1 due to hiatuses in its sediment sequence. We did not analyse enough samples of this phase in PRD-2 to subdivide it according to the chemistry of the SOM. Carbon concentrations increase towards values exceeding 10% (Fig. 3), and coarse material is generally less abundant than in earlier phases. The SOM of Phase V is characterised by a relatively constant large contribution of homoaromatic pyrolysis products (~30%) and products of degraded organic matter. Primary organic matter derived from polysaccharides and lignin is still negligible.

The characteristics of Phase V are in line with abundant anthracological and palynological evidence of increasing burning frequencies in the (Early) Neolithic (*c*. 6300–5300) in Europe (Spain: Carrión and van Geel, 1999; Santos et al., 2000; France: Carcaillet, 1998; Carcaillet et al., 2002; Switzerland: Tinner et al., 1999; Hajdas et al., 2007; Germany: Clark et al., 1989; Gerlach et al., 2006; Eckmeier et al., in press), of which plentiful proof (above all synchronous arrival of cereal pollen) for an anthropogenic cause is available (reviewed by Carcaillet et al., 2002). Pollen and charcoal records from central Europe showed that a period of deforestation occurred around 6000 BP, connected to periods of increased vegetation burning for landscape management or agricultural purposes that prolonged well into the Bronze and Iron Age (Carcaillet et al., 2002; Gobet et al., 2003; Tinner et al., 2005). Analogously, deforestation followed by the introduction of an agricultural system that includes deliberate burning, e.g. slash-and-burn, would explain the erosion events shortly after 6200–5900 cal BP which were followed by a constant accumulation of soil enriched in BC that lasted until the Iron Age at *c*. 2000 BP. The appearance of cereal pollen around 5500 BP in various sites in NW Spain (Ramil Rego, 1993; Martínez Cortizas et al., 2005) supports the onset of cultivation in that period. However, cultural pollen indicators were not found in the studied area itself until ca. 2500 BP (Aira Rodríguez et al., 1990; A. López, pers. comm.). So, whether burning practices in the Neolithic and Bronze Age were motivated by e.g. animal husbandry, cultivation, charcoal production or ritual ceremonies (Carcaillet et al., 2002) is yet to be elucidated. Phase V coincides with accelerated acidification of the soil (Kaal et al., in press). This period marks the drastic change from altering forest vegetation to the present-day cultural landscape.

Again, macroscopic charcoal content is relatively small while the pyrolysis-GC/MS fingerprint indicates burning products are abundant and not limited to the charcoal-enriched material deposited *c*. 3500–3000 BP. The fuel of these fires was probably poorly developed vegetation communities, not forests, and therefore produced only small amounts of macroscopic charcoal.

PHASE VI – Phase VI is an episode of intensified burning that happened after 1870–1695 cal BP, probably *c*. 1500 BP. It ranges between 0.25 and 0.40 m depth in PRD-1 and 0.70–0.90 m in PRD-2. The transition between phases V and VI is marked by a line of burnt soil of reddish colour. The pyrolysis-GC/MS fingerprint of the SOM of PRD-2 from Phase VI is characterised by high benzene and benzonitrile contributions (not shown), and is depleted in phenols and C_1- and C_2-benzenes, indicative of a strong impact of fire on SOM composition. The enrichment of benzene, benzonitrile and pyridine and the depletion of C_1- and C_2-benzenes is also recognised in the SOM of PRD-1, but is somewhat less pronounced. The contribution of PAHs to the pyrolysates is not particularly large, possibly reflecting a rather low average degree of condensation of the BC that may be tentatively attributed to a low temperature of the fire. Characterised by the largest peak in macroscopic charcoal content in both soils (Fig. 3), the samples of Phase VI are likely to mirror the burning of well-developed vegetation communities, which could be indicative of a brief period of forest regrowth prior to the fire.

PHASE VII – Phase VII is a period of rapid sedimentation at site PRD-2 (55 cm) with respect to PRD-1 (15 cm). The organic matter fingerprint resembles that of Phase V: it is a mix of burning residues and degraded organic matter. However, the burnt biomass did not produce large amounts of macroscopic charcoal. Phase VII is likely to be the result of frequent anthropogenic fires of less-developed vegetation similar to the period between *c*. 6000 and 2000 BP. Lignin markers and levoglucosan have slightly larger contributions to the pyrolysates than they had in previous phases, but are still of minor importance.

PHASE VIII – The surface samples are enriched in lignin products and levoglucosan, and therefore belong to a separate phase (Phase VIII). Nonetheless, the SOM is in a highly degraded state, as the contributions of the markers of SOM degradation (furans, pyrroles, etc.) are much larger than those of intact polysaccharides or lignin. The markers of polysaccharide and lignin may represent the fresh input of present vegetation mixed with older degradation products of BC and degraded organic matter, the latter being the most important; charcoal, benzene, benzonitrile and PAHs levels are relatively low in Phase VIII (Figs. 3 and 4).

Hierarchical cluster analysis of the identified phases using the composition of their pyrolysates summarises their similarities and differences (Fig. 5). Phases I and II contain little or no BC, and are therefore different from the other phases. The SOM from phases III and IV are similar mixtures of BC-derived, degraded and ''stable'' primary SOM (lipids), albeit that the SOM of Phase III produces more benzenes and less PAHs upon pyrolysis than that of Phase IV, which may indicate a different fuel source or fire milieu. As mentioned earlier, the SOM fractions of phases V and VII are akin, containing significant amounts of BC possibly formed during relatively low-intensity fires. The SOM of Phase VIII resembles that of phases V and VII, but contains more intact polysaccharide and lignin. Finally, Phase VI is very rich in BC, possibly generated during forest fire, and is therefore differentiated from the others, but its SOM still resembles that of the other phases that contain large amounts of BC more than that of the oldest two phases corresponding to the colluviated BC-deficient saprolites.

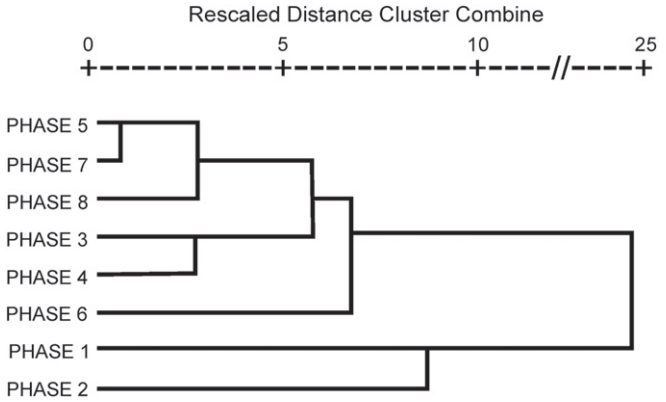

Fig. 5. Hierarchical cluster analysis of the phases identified (see Fig. 2 and Section 3.3).

These soils are not the first of its type that seem to be the result of frequent burning. The charcoals in a series of cryptopodsols from Switzerland (Blaser et al., 1997) were thought to be generated by intentional fires since the Neolithic (Tinner et al., 2005; Hajdas et al., 2007). In the dark fossil soils of the Lower Rhine Basin charred plant residues, chemically isolated as BC, were found to contribute up to 46% of the total organic soil carbon (Gerlach et al., 2006); radiocarbon ages revealed that fires responsible for this large amount of BC occurred since the Mesolithic to the Medieval period, but more intensely at the end of the Neolithic. Temperate deciduous forests rarely burn naturally, and therefore the charred material was most likely produced during anthropogenic burning (*ibid*.). The distribution of the black chernozemic soils of central Europe in general might also be attributed to prehistoric human influence like burning (Schmidt et al., 1999; Gehrt et al., 2002; Eckmeier et al., 2007). Studies developed in other areas like Australia (Skjemstad et al., 1996), South America – in particular the *Terra Preta* – (Glaser et al., 2001) and North America (Skjemstad et al., 2002; Glaser and Amelung, 2003) also attributed the use of fire in the formation of black soils, since in these soils the material from plant burning represents between 20% and 35% of the total soil carbon. The emerging picture is that vegetation fires are recorded in thick black soils, which contain the charred residues that were very likely produced by mainly anthropogenic burning. Black (colluvial) soils with a high organic matter content that started to accumulate around 6000 BP should be investigated on a possible fire driven accumulation mechanism in order to elucidate where and to what scale Neolithic burning activities changed the landscape of the Earth. It is also important to note here that our results, in agreement with those from other areas, stress the importance of human interferences in the carbon cycle at least during the last half of the Holocene. This lends support to hypothesis of Ruddiman (2003) on the role prehistorical land clearance and agriculture played in disturbing the CO_2 and CH_4 cycles since 5000 years ago.

4. Conclusions

The first Holocene fires in the investigated area of NW Spain were recorded before *c*. 8500 BP, probably during or before the Mesolithic. The fire residues of colluvial layers that formed between *c*. 8500 BP and *c*. 6000 BP (Mesolithic-Early Neolithic) produced more condensed moieties (PAHs) upon pyrolysis than after *c*. 6000 BP, possibly indicating a decline in combustion temperatures around that time. The change in fire conditions around *c*. 6000 BP coincides with the widespread intensification of anthropogenic burning activities in Europe. Periodic burning from *c*. 6000 BP onwards (Neolithic-Iron Age) culminated into the accumulation of almost two meters of BC-rich sediment.

The results match very well with the Mesolithic and Neolithic anthropogenically-driven fire record documented for central Europe. It is tempting to conclude that NW Spain should be added to the cultural landscapes formed since the Neolithic in a way similar to the history of environmental change in central Europe.

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MANUSCRIPT 4

Characterisation of aged black carbon using pyrolysis-GC/MS, thermally assisted hydrolysis and methylation (THM), direct and cross polarisation ^{13}C nuclear magnetic resonance (DP/CP NMR) and the benzenepolycarboxylic acid (BPCA) method.

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Correction: The opaque structure in Fig. 1b is referred to as a charcoal fragment, but comparison with fungal sclerotia from recent excavations suggests that it is a charred or uncharred sclerotium. cirev.2010.10.006.

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Characterisation of aged black carbon using pyrolysis-GC/MS, thermally assisted hydrolysis and methylation (THM), direct and cross-polarisation ^{13}C nuclear magnetic resonance (DP/CP NMR) and the benzenepolycarboxylic acid (BPCA) method

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ABSTRACT

Aged black carbon (BC) from biomass burning is difficult to identify chemically when it is mixed with other forms of soil organic matter (SOM). As a consequence, the natural abundance of aged and degraded BC is unknown.

We carried out a molecular characterisation of up to ~7000 yr old charcoal and NaOH-extractable SOM obtained from a colluvial soil in NW Spain using Curie point pyrolysis-GC/MS and THM. Black C was tentatively quantified using solid state ^{13}C CP and DP NMR in conjunction with a molecular mixing model (MMM), and the use of BPCAs.

Not surprisingly, the charcoal consisted for the most part of chemically distinctive BC moieties, as concluded from CP and DP NMR–MMM (>72% BC-inherent C) and the BPCA method (30–40%). Charcoal produced mainly benzene, toluene and polycyclic aromatic hydrocarbons (PAHs) upon pyrolysis and THM. The SOM was a mixture of BC-derived (producing benzene, toluene, PAHs and benzonitrile on pyrolysis) and non-BC lipid, carbohydrate and protein-derived OM. Benzenes, PAHs and benzonitrile accounted for 41–54% (pyrolysis-GC/MS) and 34–58% (THM) of total identified peak area in extractable SOM, comparable with the 32–41% BC obtained using DP NMR–MMM. Combined results suggested that the SOM BC was a partially oxidised, N-containing, weakly condensed aromatic network. Apart from increased oxidation with age, ~700 and 7000 yr old BC gave similar molecular fingerprints. The results contribute to our knowledge of the chemistry of BC, a potential climate mediator, and its fate in the terrestrial environment.

1. Introduction

Charred solid residues remaining after biomass burning are collectively referred to as black carbon (BC). Globally, the burning of 2–4 million km^2 of land produces roughly 50–270 Tg of BC $year^{-1}$ (Kuhlbusch and Crutzen, 1995; Jain, 2007). Depending on the extent of thermal alteration, BC particles can take any form along a continuum from weakly charred plant material through charcoal to soot (Masiello, 2004). BC is considered as one of the most recalcitrant forms of organic C on Earth (Schmidt and Noack, 2000) and so constitutes a significant C sink with a

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potential role in the global C cycle (Goldberg, 1985). Its importance as a C sink depends on its capacity to accumulate in the environment, which largely depends on its degradability.

Though formerly considered as inert in (bio)geochemical processes, BC degradation was revealed by its presence in dissolved organic matter (Kim et al., 2004; Kramer et al., 2004; Hockaday et al., 2006), the coating of its surfaces by bacteria and fungi (Pietikäinen et al., 2000; Hockaday et al., 2007) and mineralisation in incubation experiments (Baldock and Smernik, 2002; Hamer et al., 2004). It seems that the initial chemical alteration induced by biological or abiotic attack are depolymerisation and surface oxidation, thereby producing oxidised weakly condensed aromatic structures (Knicker et al., 2006; Knicker, 2007; Cheng et al., 2006). Degraded BC is therefore chemically similar to the highly aromatic components of 'humic substances' extracted from soils (Kumada, 1983; Haumaier and Zech, 1995), also known as Type A humic acids. Despite recent efforts (Skjemstad et al., 1996; Golchin et al., 1997; Schmidt et al., 1999; Kramer et al., 2004; Shindo et al., 2004; Hockaday et al., 2006), the contribution that BC makes to humic substances has not been proven or quantified. Hence, a global inventory of the BC stored in soil is not yet possible.

In oxic soils, the resistance of depolymerised and oxidised BC to mineralisation depends on the characteristics of the soil in which it is stored (Czimczik and Masiello, 2007). Particularly relevant to the present study is the protective effect of reactive minerals such as Fe and Al (oxy) (hydr)oxides, which probably form organomineral complexes with oxidised BC, thereby masking the functional groups on which microbial attack is focussed (Glaser et al., 2000; Brodowski et al., 2005a; Czimczik and Masiello, 2007). Incorporation of degraded or microscopic BC into microaggregates may also improve its stability (Skjemstad et al., 1996; Simas et al., 2005). However, the details of BC stabilisation are unknown because its identification often requires it to be distinguished from non-BC OM, which becomes increasingly difficult as BC ages.

Thus, the problems in elucidating the fate of BC originate from the lack of a standardised approach to identify and quantify it. Applying various methodologies to quantify the content in soils (principally photochemical, thermal and chemical oxidation techniques) to a diverse set of reference materials, Hammes et al. (2007) concluded that each method assesses different fractions of the BC continuum and that the methods are not systematically related. The majority are based on the removal of non-BC, followed by quantification of the residue as BC, and do not provide information on the chemistry of this residue. In addition, most characterisation studies are concerned with recent natural or laboratory-produced BC, while the degradation products may have a different composition and require different approaches (Cohen-Ofri et al., 2006).

Pyrolysis-GC/MS and also THM may appear inadequate for the study of BC because an unknown fraction does not produce GC-amenable products upon pyrolysis (Poirier et al., 2000; González-Vila et al., 2001; González-Pérez et al., 2004; Knicker et al., 2005) and because two thermal modifications that may be difficult to distinguish are involved (natural fire initially and pyrolysis during analysis). Nevertheless, Pastorova et al. (1994) and Boon et al. (1994) successfully applied pyrolysis-GC/MS to investigate the effect of laboratory charring on cellulose. Also, the presence of PAHs in SOM pyrolysates is usually considered as testimony of burning (Naafs, 2004; Ross et al., 2005; Rumpel et al., 2007), although small amounts of these may be secondary pyrolysis products of fatty acids (Saiz-Jiménez, 1995). The pyrolysis-GC/MS and THM signatures of various types of BC reference materials were vastly different from that of potentially interfering uncharred structures such as melanoidins (de la Rosa, 2007; de la Rosa et al., 2008). When used together, potential bias associated with the structural selectivity of pyrolysis-GC/MS and THM can be recognised (Chefetz et al., 2002). Thus, careful examination of pyrolysis and thermochemolysis products may allow identification of BC in complex OM mixtures.

Pyrolysis-GC/MS and THM were used in this study to assess the molecular composition of ca. 700 to >7000 yr old charcoal fragments (>2 mm) and NaOH-extractable SOM obtained from a colluvial soil from NW Spain. Analysis of charcoal allowed identification of typical BC products in pyrolysis-GC/MS and THM. These indicators were later used to distinguish BC from other forms of OM in SOM. In addition, the BPCA method (Glaser et al., 1998; Brodowski et al., 2005b) and solid state ^{13}C NMR were employed for quantification of BC. Micrographs obtained using scanning electron microscopy (SEM) and photographs of thin sections are presented for illustrative purposes.

The aim of the study was to identify and characterise aged BC in charcoal and NaOH-extractable SOM from the same samples. Potential advantages and disadvantages of pyrolysis-GC/MS, THM, solid state ^{13}C NMR and the BPCA method are discussed.

2. Experimental

2.1. Study site

The studied soil is a haplic Umbrisol (humic/alumic) (IUSS-ISRIC-FAO, 2006) that formed during more than 8500 yr colluviation (Costa Casais et al., 2008). Multiple erosion/sedimentation cycles give such soils a complex stratigraphy (Mücher et al., 1972). The soil type was traditionally referred to as Atlantic ranker and is characterised by a high OM content that is thought to have resisted biodegradation through sorptive protection by poorly crystalline Al phases (Carballas et al., 1978). However, the presence of BC may be a complementary cause for the slow decomposition of OM in such soil (Kaal et al., 2008a).

The soil (PRD-1) is a 1.5 m thick colluvium located in Campo Lameiro (NW Spain), 25 km to the east of the Atlantic Ocean, in an isolated hill at 320 m.a.s.l. A monolith was obtained on a recently opened trench and sliced into 5 cm sections. A selection of physicochemical properties of the samples chosen for detailed analysis (with increasing depth/age: samples 3, 14, 15, 19 and 22) is presented in Table 1. The table includes radiocarbon ages obtained from

the acid-alkaline-acid extractable OM in the fine earth fraction (Ångström Laboratory, Uppsala, Sweden). Macroscopic charcoal (>2 mm), allegedly of the same age as the soil material with which it was co-deposited (Kaal et al., 2008b), was separated from the fine earth fraction by wet sieving.

2.2. Extraction and purification of SOM

Because of the low signal intensity of pyrolysis-GC/MS obtained from whole samples, SOM was separated from the fine earth fraction by extraction with 0.1 M NaOH (10 g soil:50 ml NaOH aq.) for 5 min (2×) and water (3–5×, until the supernatant was colourless; Nierop et al., 2001). Decanting of extracts was always preceded by centrifugation (~1000*g* 15 min). The extracts were combined and acidified to pH 1.5–2.0 with HF/HCl (0.3/0.1 M) solution. Small amounts of fine roots and small charcoal particles (63 μm–2 mm) were removed from the resultant suspensions with a 63 μm mesh sieve. The sieved suspensions were dialysed against distilled water and freeze dried. As calculated from the differences in C content (dry combustion elemental analysis) of the fine earth fraction and the residue after extraction, the proportion of extractable C ranged from 60% to 92% of total soil C (Table 1). The extraction yields are slightly overestimated as the C in fine roots and 63 μm–2 mm sized charcoals was not taken into consideration. Note that extracts were not filtered, so that some particulate organic matter may be included in the SOM.

2.3. Pyrolysis-GC/MS and THM

The extractable SOM was pyrolysed using a Horizon Instruments Curie-point pyrolyser (Curie temperature of wire 600 °C) connected to a Carlo Erba GC 8000 gas chromatograph. The pyrolysis products were separated on a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51b (film thickness 0.40 μm), with He as carrier gas. The initial oven temperature was 40 °C and the heating rate was 7 °C min^{-1}. The final temperature of 320 °C was maintained for 20 min. The GC column was connected to a Fisons MD 800 mass spectrometer (*m/z* 45–650, cycle time 1 s, electron ionisation, 70 eV).

The 94 pyrolysis products used for quantification accounted for all the major peaks in the total ion current (TIC) traces. They were generally quantified on the two most abundant fragment ions using the quantification option in the MassLab 1.2.7 software.

The THM technique, also referred to as thermochemolysis, was performed as for pyrolysis-GC/MS, but with addition of a few droplets of 25% tetramethylammonium hydroxide (TMAH) in water to the sample and evaporation of the water under a 100 W halogen lamp prior to pyrolysis. Applying THM, hydrolysable bonds are transmethylated or cleaved and free carboxyl and hydroxyl groups are methylated in situ to the corresponding methyl esters and methyl ethers (Challinor, 2001). Chromatograms were quantified on 122 products. Two compounds revealing fragment ions *m/z* 91 and 155, possibly derived from an aromatic S-containing amide (NIST library), could not be explained and were omitted from the discussion.

The macroscopic charcoal (>2 mm) was ground and the pyrolysis-GC/MS and THM chromatograms were quantified as described above for the SOM. Aliquots of acetone had to be added to the charcoal in order to obtain a good coating of the ferromagnetic wires.

The resultant datasets are quantitatively biased because each compound has a different MS response factor. Nonetheless, the differences between samples analysed in a consistent manner can be used to identify compositional differences.

2.4. Solid state ^{13}C NMR

Solid state ^{13}C CP and DP NMR spectra were acquired with MAS at a ^{13}C frequency of 50.3 MHz using a Varian Unity 200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end caps and spun at 5000 ± 100 Hz in a Doty Scientific MAS probe. A 1 ms contact time was used and 4000 transients were collected for each spectrum. The length of the recycle delay was defined for each sample using an inversion recovery

Table 1
Sample properties

Sample	3	14	15	19	22
Depth [cm]	10–15	65–70	70–75	90–95	107.5–112.5
Radiocarbon age [2σ cal yr BP]	700[a]	3000[a]	3160–3360[b]	5935–6200[b]	7200[a]
Fine earth fraction (F)					
pH–H_2O	4.7	4.8	4.9	5.1	5.1
C [g kg^{-1}]	79	84	91	21	23
Molar C/N	18	17	16	15	31
Soil organic matter (S)					
Extraction yield [% of total C]	60	82	85	92	91
C [g kg^{-1}]	198	289	274	171	155
Molar C/N	20	21	19	22	21
Macroscopic charcoal (C)					
Content [g kg^{-1} bulk soil]	1.8	2.4	2.3	0.5	1.1
C [g kg^{-1}]	558	423	457	300	360
Molar C/N	260	167	255	181	204

[a] Age estimated from dated samples above and/or below.
[b] Measured ^{14}C age.

pulse sequence and multiplying the recovery time when signal intensity passed through the null by a factor of 10. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Spin lattice relaxation in the rotating frame ($T_{1\rho}H$) values were measured for each sample using a variable spin lock pulse sequence. The $T_{1\rho}H$ values were used together with the total signal intensity acquired between 300 and −50 ppm to calculate the observability of carbon in each sample using the cross polarisation ($CP–C_{obs}$) and direct polarisation ($DP–C_{obs}$) pulse sequences (Baldock and Smernik, 2002). The relative allocation of signal intensity to eight regions (alkyl 0–45 ppm; *N*-alkyl/methoxyl 45–60 ppm; *O*-alkyl 60–95; di-*O*-alkyl 95–110 ppm; aryl 110–145 ppm; *O*-aryl 145–165 ppm; amide/carbonyl 165–190 ppm and ketone 190–215 ppm) was determined after reallocating signal intensity from spinning side bands back to their parent resonances (Baldock and Smernik, 2002). The relative signal intensities obtained from the CP and DP spectra were used in conjunction with a MMM (Baldock et al., 2004) to estimate the molecular composition of the organic materials in the samples.

2.5. BC analysis using the BPCA method

BC content of the charcoals and fine earth fraction (<2 mm) was determined as described in Brodowski et al. (2005b); insufficient extracted SOM was available for analysis. Briefly, metal elimination was achieved by digesting soil or charcoal with 4 M CF_3CO_2H acid. The residue was collected by filtration and subjected to high pressure digestion with 14.3 M HNO_3 at 170 °C for 8 h. Thereby, BC was oxidised to BPCAs. The solution was diluted to 10 ml, an aliquot of 2 ml was taken, diluted and 100 μg of citric acid added as internal standard. The solution was cleaned using cation exchange resin (Dowex 50 W × 8, 200–400 mesh, Fluka, Steinheim, Germany) and freeze dried. As a recovery standard, 100 μg biphenyl-2,2′-dicarboxylic acid in MeOH were used. Derivatisation of the BPCAs to trimethylsilyl derivatives with *N,O*-bis(trimethylsilyl) trifluoroacetamide was followed by analysis using an Agilent 6890N gas chromatograph (Agilent Technologies, Waldbronn, Germany) equipped with a flame ionization detector and SPB-5 capillary column. The BPCA carbon yields from BPCAs with 3 to 6 carboxyl groups were multiplied by a correction factor of 2.27 for BC content estimation (Glaser et al., 1998). This factor provides a conservative minimum estimate of BC content of soil (Brodowski et al., 2005b).

Table 2
Proportions (%) from CP and DP NMR (C, charcoal; S, soil organic matter; MMM, molecular mixing model; N/A, not analysed)

Method	C03	C14	C15	C19	C22	S03	S14	S15	S19	S22
CP NMR										
C observability [%]	30.8	35.4	34.3	17.6	21.9	17.5	57.4	20.3	13.4	15.2
Alkyl	3.6	6.1	2.8	3.1	2.9	30.0	17.8	29.6	32.1	31.0
N-Alkyl/methoxyl	1.9	2.5	1.8	1.0	1.8	7.9	6.3	6.8	8.4	9.0
O-Alkyl	5.7	7.1	5.9	5.8	5.7	20.7	16.3	17.6	18.3	19.6
Di-*O*-alkyl	4.7	6.0	4.9	4.9	5.4	5.4	5.5	5.0	5.3	4.6
Aryl	70.5	65.7	69.2	61.7	67.7	19.3	29.1	23.7	19.0	18.1
O-Aryl	7.2	6.0	7.0	11.1	7.8	6.6	9.7	7.4	6.9	6.9
Carboxyl/amide	5.5	6.0	7.5	11.1	7.8	9.0	12.7	9.0	9.0	9.7
Ketone	0.9	0.6	0.9	1.3	1.0	1.0	2.6	0.8	1.1	1.1
CP NMR–MMM										
Carbohydrate	3.4	6.3	4.0	5.1	4.3	22.9	15.1	18.1	18.4	20.5
Protein	0.0	0.0	0.0	0.0	0.0	14.7	5.3	10.3	14.6	17.8
Lignin	0.0	0.0	0.0	0.0	0.0	19.5	23.5	18.0	23.4	22.3
Lipid	2.8	6.0	1.8	2.8	2.2	25.1	13.2	26.9	27.5	24.7
Carbonyl	2.9	4.1	7.5	17.7	9.0	4.5	19.9	6.3	4.4	4.3
BC	91.0	83.7	86.7	74.4	84.6	13.4	23.0	20.3	11.7	10.5
DP NMR										
C observability [%]	103.1	96.5	92.7	70.1	78.4	114.6	116.7	116.7	N/A	N/A
Alkyl	3.3	4.0	1.5	0.0	0.0	11.5	6.9	6.6	N/A	N/A
N-Alkyl/methoxyl	1.9	2.7	1.4	1.0	1.0	4.9	1.8	2.8	N/A	N/A
O-Alkyl	5.7	6.2	4.3	3.9	4.4	13.7	8.5	9.7	N/A	N/A
Di-*O*-alkyl	5.4	5.0	4.2	3.3	4.1	6.1	5.1	5.1	N/A	N/A
Aryl	66.4	61.2	66.3	62.3	68.3	37.3	44.0	41.8	N/A	N/A
O-Aryl	8.4	8.7	9.5	13.3	10.4	12.3	16.1	14.7	N/A	N/A
Carboxyl/amide	8.2	10.3	11.3	14.4	9.8	12.3	14.9	15.7	N/A	N/A
Ketone	0.7	2.0	1.6	1.9	1.9	1.9	2.8	3.6	N/A	N/A
DP NMR–MMM										
Carbohydrate	4.5	5.6	2.1	2.2	1.8	11.7	4.9	6.5	N/A	N/A
Protein	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0	N/A	N/A
Lignin	0.0	0.0	0.0	0.0	0.0	26.6	23.0	22.8	N/A	N/A
Lipid	2.8	2.6	0.7	0.0	0.0	8.5	3.8	3.5	N/A	N/A
Carbonyl	9.7	15.7	17.9	25.1	15.0	21.0	27.2	29.9	N/A	N/A
BC	83.0	73.5	79.4	72.7	83.2	32.2	41.0	37.3	N/A	N/A

3. Results and discussion

3.1. Macroscopic charcoal (>2 mm)

The C content of the charcoal ranged from 300 to 560 g kg^{-1} (Table 1). The content decreased with the radiocarbon age of the organic C, coinciding with a decreased C_{obs} as analysed using CP (28.0 ± 7.9%) and DP NMR (88.2 ± 13.6; Table 2). The low CP–C_{obs} of charcoal C could have resulted from either a lack of protons for ^{1}H–^{13}C cross polarisation in fused aromatic structures and/or the presence of paramagnetic materials (Smernik et al., 2002). In

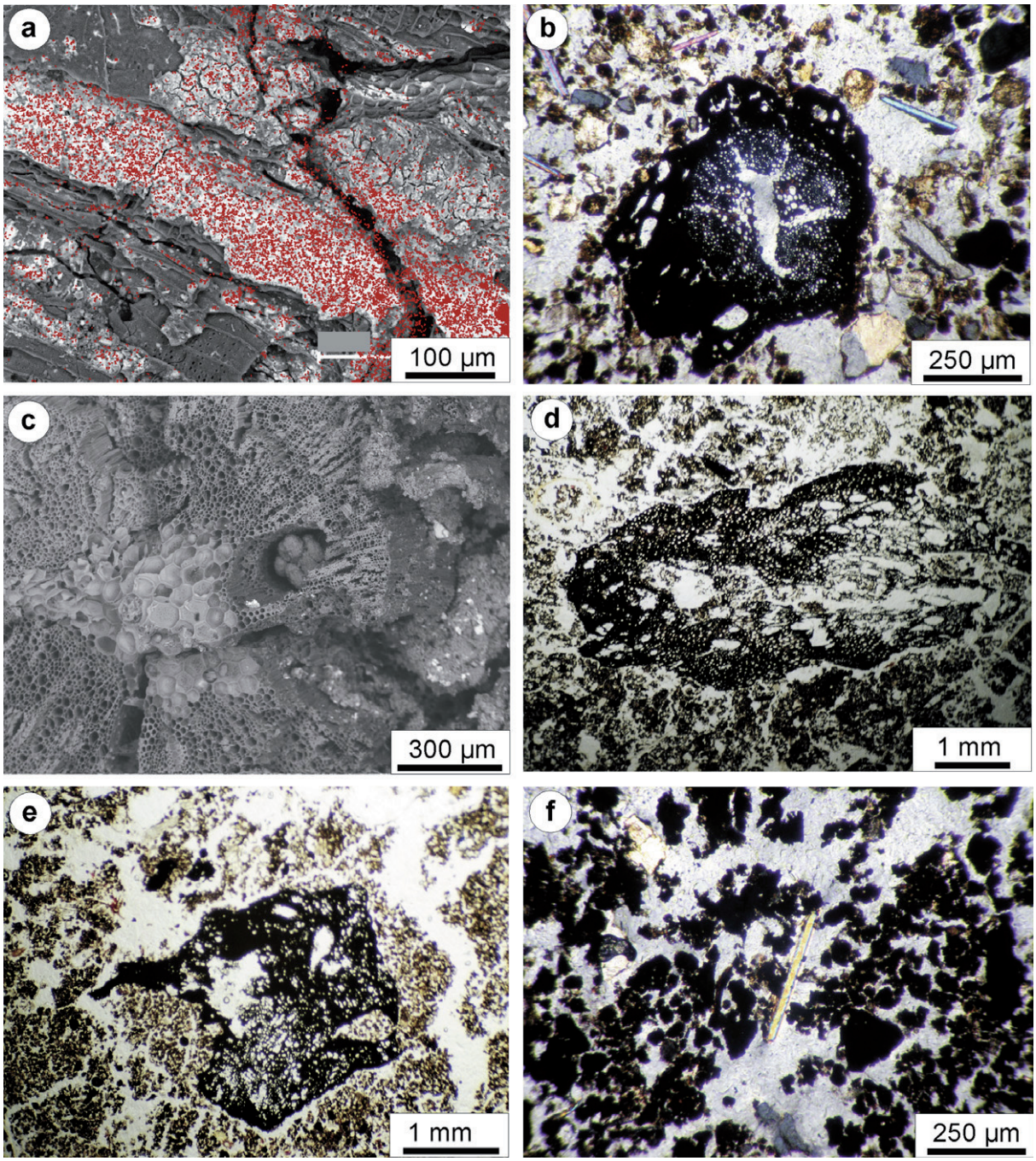

Fig. 1. (a) Micrograph of charcoal particle from sample 22 (C22) showing adsorption of Fe (oxy)(hydr)oxide (red dot map). (b) Charcoal fragment in thin section showing a degraded uncharred nucleus. (c) Micrograph of charcoal fragment showing xylophage casts next to the pith. (d) Strongly degraded charcoal fragment in thin section. (e) Strongly degraded charcoal fragment in thin section. Note the microgranular decay products on the lower right of the fragment. (f) Microgranular matrix of blackish potentially BC-derived OM (see Section 3.4).

DP NMR analysis, low observability (DP–C_{obs}) does not result from a lack of protons and can be attributed to the presence of paramagnetic species. Indeed, qualitative SEM–EDX (energy-dispersive X-ray spectroscopy) showed that charcoal surfaces and vessels were sometimes coated with Fe and Al phases (Fig. 1a). Differences between CP and DP spectra were small, with aryl C giving the strongest signal (62–71%; Table 2 and Fig. 2). The combined proportions of *O*-aryl and carboxyl/amide C (on average 15% and 21% for CP and DP NMR, respectively) were indicative of oxidation; however, a broadening of the aryl resonance due to the presence of Fe may also account for some of the signal in these two regions. Other chemical shift regions accounted for up to 7.1% of total signal intensity.

The NMR–MMM combination indicated that the charcoal consisted largely of BC (84 ± 6% and 78 ± 5% for CP and DP, respectively; Table 2). The remaining C was allocated for the most part to the 'carbonyl' end member of the MMM. This carbonyl end member is not a true biocomponent and was incorporated into the MMM to account for functional groups formed upon degradation. Taking into consideration that the contributions of biocomponents other than BC were small, the carbonyl was very likely associated with BC and so reflected BC oxidation. A progressive oxidation of BC may explain the increase in the carbonyl contribution with increasing age. The sum of carbonyl and BC (87–99%) is probably a better estimate of BC content when aged charcoal is analysed. The increase in carbonyl with age and concomitant decrease in DP–C_{obs} is tentatively interpreted as the binding of Fe to progressively carboxylated charcoal surfaces (Brodowski et al., 2005a).

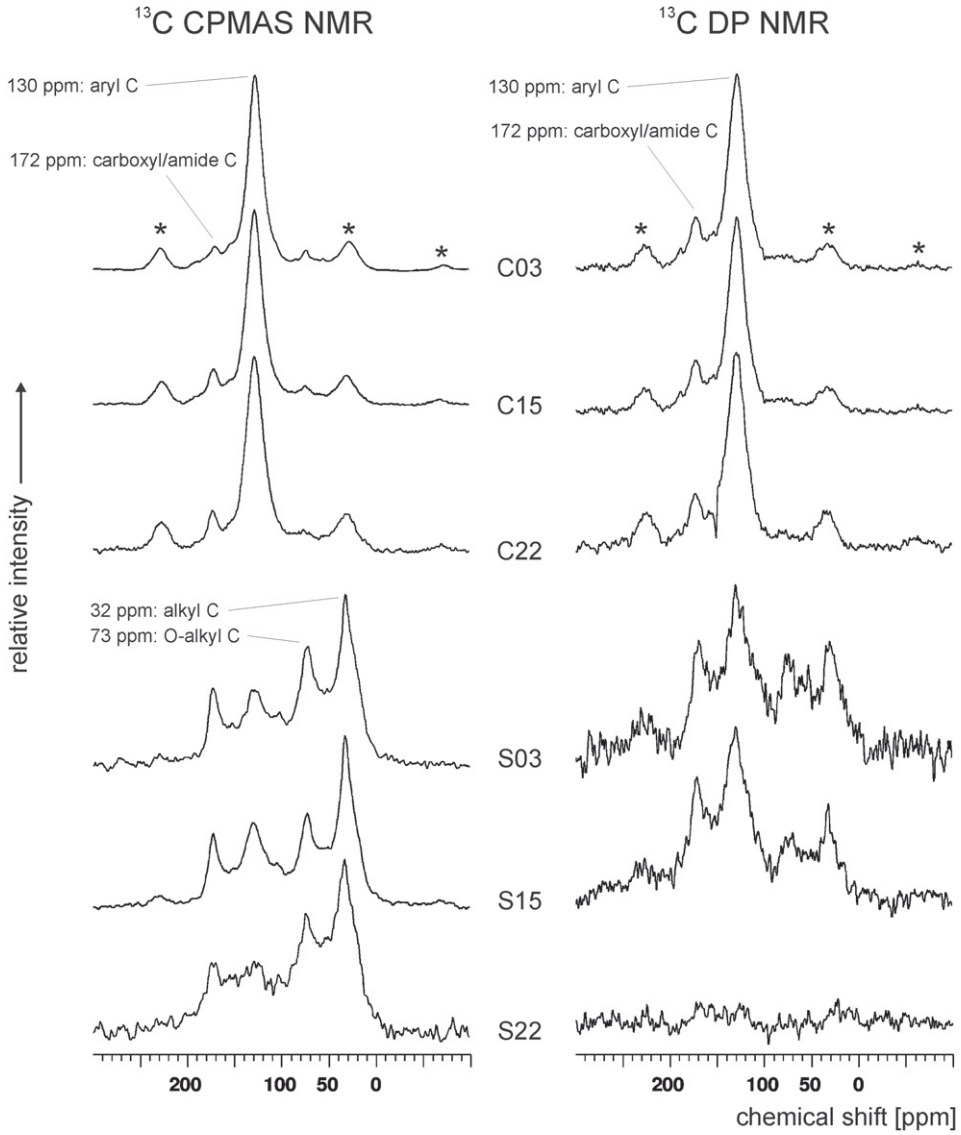

Fig. 2. ^{13}C NMR spectra of selected samples (C, charcoal; S, soil organic matter). First and second order spinning side bands of aryl C are indicated by asterisks.

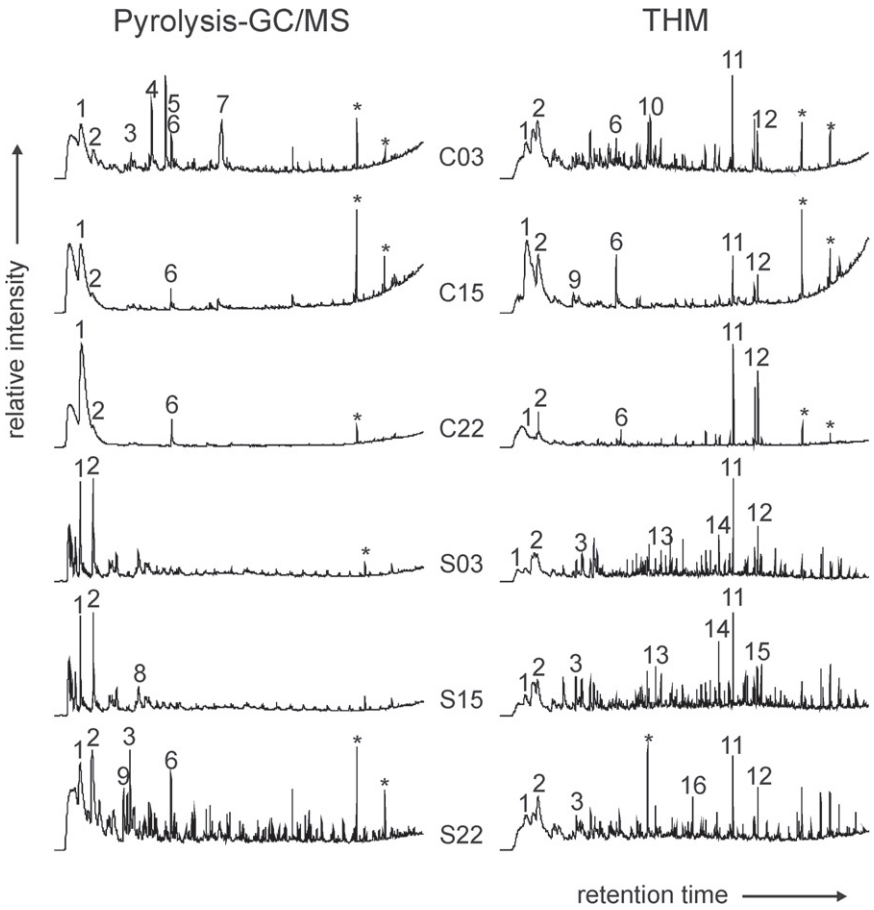

Fig. 3. TIC traces of selected samples obtained from pyrolysis-GC/MS and partial mass chromatograms (*m/z* 60–650) from THM. C, charcoal; S, soil organic matter. Compounds: 1, benzene; 2, toluene; 3, phenol; 4, levoglucosenone; 5, guaiacol; 6, naphthalene; 7, levoglucosan; 8, benzonitrile; 9, 5-methyl-2-furaldehyde; 10, xylapyranose + xylofuranoside; 11, C_{16}-FAME; 12, C_{18}-FAME; 13, B2CA; 14, B3CA; 15, B4CA; 16, benzenesulfonamide(?); ★, contamination (phthalates, squalene, TMAH byproducts).

Pyrolysis-GC/MS of the charcoal gave very large benzene contributions of up to 85% of total identified peak area (Fig. 3 and Table 3). Benzene is thus the principal pyrolysis product of charcoal BC. Additionally, significant amounts of other aromatics such as toluene, C_2 benzenes, benzonitrile and PAHs were identified. None of these pyrolysis products are true markers of BC: PAHs sometimes form upon cyclisation of fatty acids during pyrolysis (Saiz-Jiménez, 1995) and benzene, toluene and benzonitrile are also produced upon pyrolysis of, inter alia, lignin, tannin and proteins. Nonetheless, a dominance of this set of compounds is indicative of BC (Naafs, 2004; de la Rosa, 2007; Kaal et al., 2008a). In addition to the products of BC, the charcoal from sample 3 gave noteworthy peaks for guaiacols and levoglucosan, which probably originated from an uncharred lignocellulose core (cf. de la Rosa, 2007). Charcoal fragments with an uncharred partially degraded core were indeed observed in thin sections (Fig. 1b). Contrary to NMR, pyrolysis-GC/MS did not indicate significant contributions of pyrolysis products with a carboxylic group, which is a predictable effect of (1) using a non-polar GC column inadequate for the analysis of polar compounds (Dignac et al., 2006) and (2) the pyrolysis step causing decarboxylation (Saiz-Jiménez, 1994).

The THM technique, on the other hand, includes methylation of polar functional groups, thereby improving the chromatographic behaviour of polar moieties. Indeed, besides the large contribution from benzene (19–64% of total identified peak area), toluene (19–22%) and PAHs (6.4–9.5%), THM revealed a large suit of aromatic methyl ethers and methyl esters (Fig. 3 and Table 4), reflecting methylated phenolic and carboxylic arenes, respectively, that were not observed using conventional pyrolysis-GC/MS. They can be divided into three groups, viz. methoxybenzenes (0.9–14.5%), methoxybenzoic acid methyl esters (0.2–0.9%) and benzene with *n* carboxylic acid groups (B*n*CAs, fully methylated) with *n* ranging from 1 to 6 (0.1–7.8%). Phenol and methyl phenols were added to the methoxybenzenes because these products reflect incomplete methylation. The presence of B*n*CAs (Fig. 4) in the thermochemolysates is in agreement with the partially carboxylated BC inferred from NMR–MMM. Although oxidised charcoal apparently produces B*n*CAs upon THM, they cannot be considered markers, sensu stricto, as recently

Table 3
Proportion (%) of pyrolysis products (C, charcoal; S, soil organic matter)

Class	Compound (No.)	C03	C14	C15	C19	C22	S03	S14	S15	S19	S22
Benzenes		53.6	86.7	79.1	93.0	90.4	33.2	32.8	32.8	30.6	43.0
	Benzene (1)	35.7	79.8	70.4	82.8	84.9	11.1	13.2	11.3	12.1	16.8
	Toluene (1)	13.7	6.2	7.6	9.5	4.9	16.5	15.3	15.8	13.5	19.6
	C_2-benzenes (4)	4.2	0.7	1.1	0.8	0.6	5.7	4.3	5.6	5.0	6.6
PAHs (8)		4.7	5.2	5.6	4.9	5.3	5.1	4.7	5.8	8.5	6.9
Carbohydrates		22.6	0.6	4.2	0.1	0.1	23.5	24.8	25.5	19.3	19.0
	Furans (4)	5.7	0.5	0.8	0.0	0.1	17.7	17.5	19.8	15.5	15.8
	Acetic acid (1)	0.0	0.0	0.0	0.0	0.0	3.7	5.6	4.0	3.1	1.8
	Levoglucosan (1)	16.9	0.1	3.4	0.1	0.1	2.1	1.7	1.7	0.7	1.4
N-compounds		2.7	1.8	2.7	0.4	1.2	15.0	14.5	13.1	13.4	11.7
	Pyrroles (3)	0.6	0.1	0.1	0.0	0.0	4.0	3.2	2.7	2.7	2.0
	Pyridines (3)	0.4	0.1	0.2	0.1	0.0	7.4	7.9	7.1	6.6	5.6
	Indole (1)	0.0	0.0	0.0	0.0	0.0	0.4	0.3	0.4	0.4	0.2
	Benzonitrile (1)	1.7	1.6	2.3	0.3	1.1	3.1	2.9	2.9	3.5	3.7
	(*iso*)Quinoline (1)	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.2	0.1
Lignin – guaiacols (2)		2.2	0.0	0.2	0.0	0.0	0.7	0.3	0.3	0.2	0.2
Phenols (3)		7.3	1.7	1.9	0.7	1.0	14.2	10.4	13.4	10.6	9.2
Lipids (60)		7.0	3.9	6.4	0.8	2.0	8.3	12.6	9.1	17.4	10.0
BC contribution[a]		59.9	93.6	87.0	98.3	96.8	41.6	40.6	41.6	42.9	53.8

[a] ∑(benzenes, PAHs, (iso)quinoline, benzonitrile).

Table 4
Proportion (%) of THM products (C, charcoal; S, soil organic matter)

Class	Compound (No.)	C03	C14	C15	C19	C22	S03	S14	S15	S19	S22
Benzenes		46.3	73.1	76.4	85.7	45.1	20.8	25.4	29.9	50.5	48.6
	Benzene (1)	19.7	47.2	53.8	63.9	19.9	8.1	8.4	11.6	14.3	15.8
	Toluene (1)	19.3	21.8	20.6	19.3	20.7	9.2	12.1	13.1	26.6	21.9
	C_2-benzenes (4)	5.3	3.1	1.6	2.1	3.5	2.7	4.1	4.0	7.6	8.3
	C_3-benzenes (4)	2.0	0.9	0.4	0.4	0.9	0.8	0.8	1.3	2.0	2.5
PAHs (19)		8.3	9.5	7.8	8.7	6.4	4.8	3.4	6.6	4.3	7.2
O- and OCH_3-benzenes (17)		14.5	4.0	2.2	0.9	5.5	11.1	7.6	15.2	10.1	13.1
Methoxybenzoic acids (6)		0.9	0.4	0.3	0.2	0.2	6.2	5.2	3.1	0.7	0.8
B*n*CA		6.4	0.9	1.4	0.1	7.8	14.2	4.7	13.7	1.6	1.3
	B1CA (1)	0.6	0.1	0.3	0.0	1.4	4.6	1.8	2.0	0.8	0.5
	B2CA (3)	1.2	0.1	0.2	0.0	1.0	2.6	1.7	2.2	0.2	0.3
	B3CA (3)	2.2	0.4	0.6	0.1	2.9	4.2	0.8	4.9	0.3	0.3
	B4CA (3)	2.1	0.3	0.3	0.0	2.2	2.6	0.4	4.3	0.2	0.1
	B5CA (1)	0.3	0.0	0.0	0.0	0.2	0.2	0.0	0.4	0.0	0.0
	B6CA (1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbohydrates		3.6	0.1	0.1	0.0	1.1	13.9	8.9	7.4	2.5	3.1
	C_4–C_5-diacids (4)	0.8	0.1	0.1	0.0	1.1	10.4	8.5	6.4	2.5	3.0
	Levo- and xylosugars (5)	2.8	0.0	0.0	0.0	0.0	3.2	0.3	0.6	0.0	0.0
	Cyclopentatrione (1)	0.0	0.0	0.0	0.0	0.0	0.3	0.1	0.4	0.0	0.1
N-compounds		11.0	8.4	7.0	4.1	9.0	5.2	4.0	7.0	10.2	11.3
	Pyrroles (4)	8.1	4.7	3.0	1.4	7.9	3.4	2.7	4.7	8.8	9.5
	Pyridiminedione (1)	0.2	0.0	0.0	0.0	0.1	0.9	0.8	1.0	0.9	0.8
	Benzonitrile (1)	2.7	3.8	4.0	2.7	1.0	0.9	0.5	1.3	0.5	1.0
Lipids		9.1	3.5	4.7	0.3	24.9	23.9	40.8	17.1	20.1	14.7
	$<C_{20}$ FAMEs (13)	8.6	3.1	4.3	0.3	24.1	15.5	20.3	9.4	11.4	8.2
	$>C_{20}$ FAMEs (11)	0.5	0.4	0.4	0.0	0.8	5.1	16.0	5.8	7.9	5.9
	ω-Methoxy FAMEs (9)	0.0	0.0	0.0	0.0	0.0	2.2	2.7	1.2	0.6	0.4
	DAMEs (6)	0.0	0.0	0.0	0.0	0.0	0.5	0.8	0.3	0.3	0.3
	Cutin markers (2)	0.0	0.0	0.0	0.0	0.0	0.5	1.0	0.4	0.0	0.0
BC contribution[a]		63.7	87.3	89.7	97.2	60.3	40.6	34.0	51.5	56.8	58.0

All acids identified as Me esters.
[a] ∑(benzenes, PAHs, B*n*CA, benzonitrile).

demonstrated by Dickens and coworkers (2007). Apart from aromatics, the charcoal produced a significant amount of plant-derived, ester-bound lipids (up to 25%), dominated by a homologous series of C_9–C_{30} fatty acid methyl esters (FAMEs; 96–99% of total lipid products). The large contribution of lipids to the charcoal of sample 22 was not confirmed with any other method and may have been an analytical artefact. Carbohydrate-derived THM products were very scarce, if present at all (0.0–3.6%), but THM is known to be relatively insensible to carbohydrate analysis (e.g., Nierop and Buurman, 2007). The xylosugars were concentrated in the sample with the

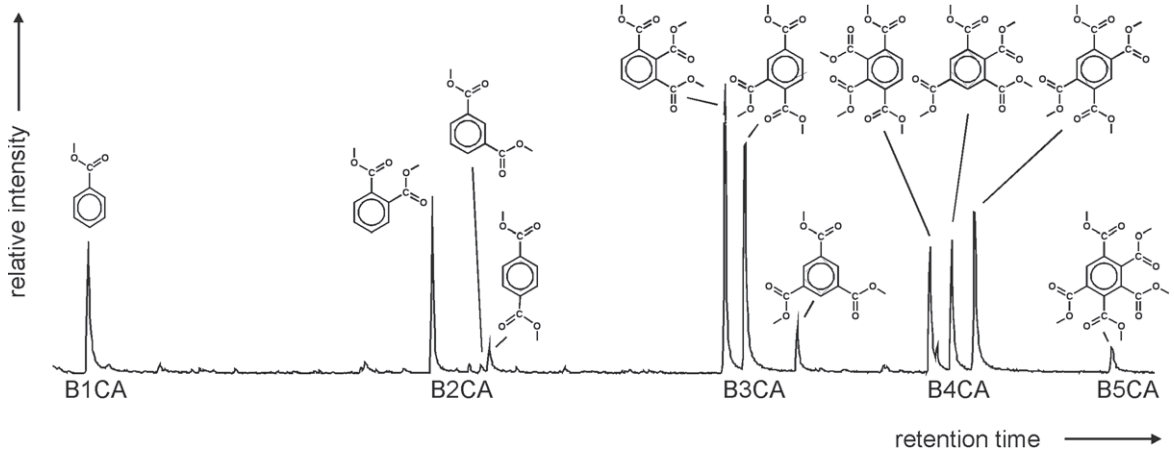

Fig. 4. Partial mass chromatogram (*m*/*z* 105 + 163 + 221 + 279 + 337 + 395) showing B*n*CAs in thermochemolysate from charcoal of sample 22 (see text).

uncharred core (C03). Cyclopentenones, common THM products of carbohydrates, were not observed. The low contents of lipid and carbohydrate products probably reflected the presence of small amounts of weakly or non-charred biomass or tar produced during charring.

While NMR–MMM, pyrolysis-GC/MS and THM suggested the charcoal samples consisted almost completely of BC, the BPCA method provided BC concentrations of only 30–40% of total C (Table 5). It is possible that the conversion factor of 2.27 is too low for aged and significantly degraded charcoal. This conversion factor was introduced by Glaser et al. (1998) to account for BC-inherent C evolving as CO_2 during the oxidation to BPCAs. The BPCA method assesses only highly condensed BC (Hammes et al., 2007), so that progressive depolymerisation of BC during storage in soil should produce a decline in BPCA yield. In the present study, depolymerisation and the low BPCA yield may be related to partial oxidation (NMR–MMM, THM) and biological degradation (as exemplified by Fig. 1c–e). The 'true' conversion factor may therefore be larger for this type of charcoal.

The results for the charcoal are in line with previous NMR (Skjemstad et al. 1999; Baldock and Smernik, 2002) and pyrolysis-GC/MS studies (Naafs, 2004; de la Rosa, 2007).

3.2. Extractable SOM

The CP–C_{obs} of the extracted SOM fraction was very low (10–60%; Table 2). Using CP, alkyl C contributions were largest, followed by aryl and *O*-alkyl C (Fig. 2). However, the DP NMR showed that the extractable SOM-C was predominantly aryl, *O*-aryl and carboxyl/amide C (Table 2). Thus, a significant portion of aromatic SOM was observed with DP but not with CP NMR. NMR–MMM of the apparently biased CP NMR data erroneously suggested that the SOM was a mixture of similar amounts of lignin, lipid, carbohydrate and BC. Using the quantified DP spectra for MMM mixing, BC was the dominant component (32–41%), followed by carbonyl and lignin. Only three of the five extractable SOM samples gave meaningful spectra, but DP NMR–MMM analysis of three additional SOM samples (25–40 cm depth) gave similar BC content of 43 ± 2% (not shown). Part of the signal allocated to lignin and carbonyl with the MMM model may reflect oxidised BC because lignin markers in the pyrolysates (see below) were negligible. Incorrect allocation of *O*-aryl C to lignin requires methoxyl C in the 45–60 ppm region that could actually be the *N*-alkyl C moiety of protein. If this is the case, the MMM mistakenly translated *O*-aryl and *N*-alkyl C intensity to lignin while it actually represented

Table 5
BPCA carbon yield from charcoal (C) and fine earth fraction (F)

Charcoal	C03		C14		C15		C19		C22	
	g C kg^{-1} C	SE	g C kg^{-1} C	SE	g C kg^{-1} C	SE	g C kg^{-1} C	SE	g C kg^{-1} C	SE
BC										
Without CF[a]	140.6	1.7	166.0	22.3	156.3	5.3	152.3	24.9	151.9	25.0
With CF[a]	318.9	3.9	376.4	50.6	354.4	11.9	345.3	56.5	344.5	56.6
Fine earth										
	F03		F14		F15		F19		F22	
	g C kg^{-1} C	SE[a]	g C kg^{-1} C	SE	g C kg^{-1} C	SE	g C kg^{-1} C	SE	g C kg^{-1} C	SE
BC										
Without CF[b]	63.6	11.1	79.1	18.5	63.2	11.7	118.5	18.4	91.8	0.0
With CF[b]	144.2	25.1	179.4	41.9	143.3	26.6	268.6	41.7	208.2	0.0

[a] Standard error (n = 2).
[b] CF, correction factor 2.27 (Glaser et al., 1998).

resonance of functionalised BC and proteins. These results are strong evidence for a major contribution of partially oxidised BC to the SOM fraction.

Pyrolysis-GC/MS of the SOM produced predominantly benzenes and furans (Fig. 3 and Table 3). Straight chain *n*-alkane/alkene pairs, N-containing pyrolysis products (pyrroles, pyridines, benzonitrile), phenol and PAHs were also abundant. Lignin derivatives (methoxyphenols) were almost absent, which is indicative of charring (Almendros et al., 1992). Benzene, toluene, benzonitrile, (iso)quinoline and PAHs most likely derived from pyrolysis of BC, as mentioned earlier for charcoal. N-containing pyrolysis products were less abundant in the pyrograms from charcoal because wood contains relatively little N (C/N ratio, Table 1). Additional N may be present in amide moieties, but not found because the amide group is often dehydrated during pyrolysis. In this study, the furans, pyrroles and pyridines were for the most part derivatives of degraded carbohydrates and proteins (Kaal et al., 2008a). Benzenes, PAHs, benzonitrile and (iso)quinoline (41–54%) could be indicative of BC when pyrolysis-GC/MS is applied to complex mixtures such as SOM. We have to keep in mind that these products are not markers of BC; pyrolysis-GC/MS cannot be used to ascertain low BC concentration (< ~1–5% of the C), because other biocomponents would then account for a significant portion of (especially) the benzene and toluene produced.

The extracted SOM afforded large amounts of benzenes upon THM (Fig. 3 and Table 4; 35 ± 14%). Other homocyclic aromatic compounds were PAHs (5.2 ± 1.6%), methoxybenzenes (11.4 ± 2.9%), methoxybenzoic acids (3.2 ± 2.5%), B*n*CAs (7.1 ± 6.4%) and benzonitrile (0.8 ± 0.4%). The benzenes, PAHs, B*n*CAs and benzonitrile most likely derived from BC. These thermochemolysis products together accounted for 34–58% of total identified peak area, which is an estimate of BC contribution to the total set of THM products. Compared to charcoal, the SOM was enriched in long chain FAMEs (C_{20}–C_{30}), ω-methoxy FAMEs and dimethyl esters of α,ω-diacids (DAMEs) after THM (6–20% against <1% in charcoal). These compounds allegedly derived from suberin, i.e. an ester-bound biopolymer consisting of an aliphatic and an aromatic domain, concentrated in roots and bark (Kolattukudy, 2001; Nierop et al., 2003). Finally, THM afforded 2–14% carbohydrate-derived compounds, predominantly butanedioic acid and butenedioic acid (dimethyl ester).

The pyrolysis and THM products were much more diverse for the SOM than for the macroscopic charcoal specimen. In general, only PAHs, benzene, toluene (pyrolysis-GC/MS and THM) and some B*n*CAs (THM only), had greater contributions in the charcoal than in the SOM. This is the set of compounds that was suggested to be characteristic of BC (Kaal et al., 2008a) and was used for estimating the contribution of BC derivatives in the present study.

3.3. Fine earth fraction (BPCA method only)

The total C in the fine earth (Table 1) consisted of 14–27% BPCA-C (Table 5). For all samples except sample 3, extraction yield exceeded 80% of the C present in the fine earth (Table 1). Thus, the small BC content obtained using the BPCA method cannot be explained by the non-extractability of non-BC structures. The BPCA method probably underestimated BC content because it only takes highly condensed aromatics into account. We believe the conversion factor used to convert BPCA-C yield to BC content (2.27) should be greater for ancient and degraded BC samples, supporting the proposition that this factor gives a minimum estimate for BC concentration (Brodowski et al., 2005b). Nonetheless, even though the BPCA method lacks BC-type specific conversion factors for the various types and degrees of degradation of BC, it provides proof as to whether aromatic C structures seen by the other methods originate from BC or not.

3.4. Synthesis

Application of a diverse suite of molecular characterisation methods has not till now been applied to ancient charcoal and extractable SOM partially originating from BC. The results of ^{13}C DP NMR–MMM and the BPCA method provided unambiguous evidence of the presence of BC in the SOM. Results of pyrolysis-GC/MS suggested that BC can be recognised by way of high peak intensities for benzene, toluene, benzonitrile and PAHs. Additionally, as shown from NMR–MMM and THM, in both charcoal and SOM oxidised BC moieties were present. The relatively low yield of BC using the BPCA method suggested a rather depolymerised BC. From these results we conclude that the BC in the soil is a partially oxidised, highly aromatic, but weakly condensed network, containing significant amounts of N. This conclusion supports the model of BC recently suggested by Knicker (2007).

In the soil, many degraded charcoal fragments were found. Preliminary micromorphological studies showed that BC was present in distinct charcoal particles but also in dark and often blackish microaggregates comprising coalesced BC remnants and microscopic charcoal (Fig. 1f). Intimate association with 'active Al' hydroxides protecting the functionalised BC may explain why the BC or degradation products of BC were not mineralised after ~7000 yr storage (Czimczik and Masiello, 2007; Kaal et al., 2008c).

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MANUSCRIPT 5

Micromorphological evidence of black carbon in colluvial soils from NW Spain.

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European Journal of Soil Science 59, 1133-1140.

Correction: The scale bar in Figure 1f (250 μ) is reported to apply to all images in Figure 4, but in Figures 4a-c this scale bar would correspond to approximately 1 mm instead. uascirev.2010.10.006.

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Micromorphological evidence of black carbon in colluvial soils from NW Spain

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Summary

Biomass burning produces a residue called black carbon (BC). Black C is generally considered to be highly resistant against biodegradation and has a potential role in the global C cycle, but is difficult to identify and quantify when subjected to prolonged degradation in terrestrial sediments. The colluvial soils from Campo Lameiro (NW Spain), also known as 'Atlantic rankers', are rich in organic matter (up to 140 g C kg^{-1} soil). A micromorphological study was undertaken to test the hypothesis that a large proportion of the organic matter was derived from BC formed during Holocene wildfires (up to > 6000 years ago).

As roughly estimated from image analysis of 12 thin sections, the volumetric BC contribution ranged between 10 and 60% (26% on average) of the organic matter. This is a conservative estimate as additional morphologically unrecognizable BC was present in the microgranular matrix of coalesced excrement. We conclude that (i) currently unknown quantities of BC are stored in Atlantic rankers and (ii) analysis of thin sections is an effective tool to identify BC.

Introduction

The colluvial soils of Galicia (NW Spain) are deep, dark and rich in organic matter. Holocene changes in landscape stability produced a complex stratigraphy of colluviated A horizons and stone layers (Mücher *et al*., 1972; van Mourik, 1999). These haplic Umbrisols (humic/alumic) (International Union of Soil Sciences – ISRIC World Soil Information – FAO, 2006) were traditionally referred to as Atlantic rankers, humiferous Atlantic soils, aluminic soils and aluandic acid soils (Carballas *et al*., 1978; Duchaufour, 1982; Macías *et al*., 1982; García-Rodeja *et al*., 2004). Galician Atlantic rankers develop in the sesquioxide-rich weathering products of granite and schist. Once released from the parent rock, the Al (and Fe) is sorbed/complexed by abundant organic matter, which is thought to inhibit the crystallization of Al and slow decomposition of the organic matter through protective mechanisms (Carballas *et al*., 1979; González-Prieto *et al*., 1992).

Black carbon (BC) is a collection of highly aromatic solid residues from burning, including charcoal and soot. The assumed recalcitrance of BC is currently being questioned now that loss processes in soil are being demonstrated (Masiello, 2004; Hockaday *et al*., 2006; Czimczik & Masiello, 2007). Nonetheless, as a general rule, BC is much more resistant against biodegradation than non-charred plant remains and therefore a potential sink of C in soils (Goldberg, 1985; Kuhlbusch & Crutzen, 1995). The lack of a widely accepted standardized method for BC quantification slows down progress in our understanding of BC and its role in C cycling (Hammes *et al*., 2007). Increasing evidence shows that a significant proportion of highly aromatic 'humic substances' may originate from BC (Kumada, 1983; Haumaier & Zech, 1995; Schmidt *et al*., 1999; Shindo *et al*., 2004). Although future estimates of the global amount of BC in soil depend on the abundance of these humic substances, it is extremely difficult to prove that they are derived from BC. Recently, a colluvial soil (Atlantic ranker) was shown to contain significant amounts of BC (Kaal *et al*., 2008a). This conclusion was drawn from the large proportion of benzenes and polycyclic aromatic hydrocarbons (PAHs) in pyrolysis-GC/MS chromatograms and aryl C in solid-state ^{13}C cross-polarisation nuclear magnetic resonance (CP NMR) spectra, both obtained from NaOH-extractable organic matter. Nonetheless, more evidence for the presence of BC is needed because pyrolysis-GC/MS and ^{13}C CP NMR have significant limitations in the study of BC (Schmidt *et al*., 1999; Poirier *et al*., 2003).

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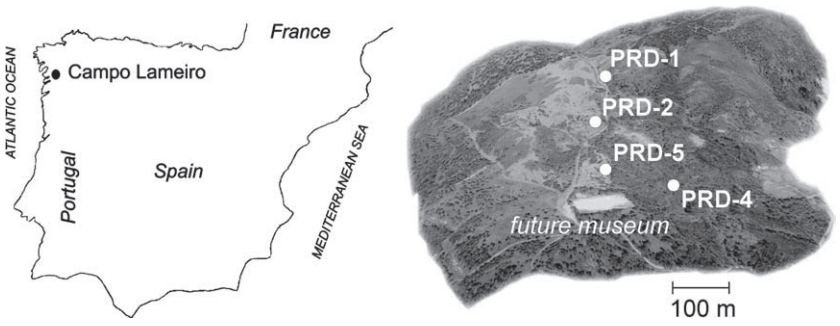

Figure 1 Location of the study area.

Micromorphology, i.e. the microscopic analysis of thin sections, reveals structural characteristics of the various organic matter forms present in soil, and their association with inorganic soil constituents. Micromorphology is unparalleled in its capacity to provide information about the structure and often the origin of organic matter in terrestrial soils, including BC (Hedges *et al.*, 2000). The present micromorphological study identifies and describes ancient BC and estimates its contribution to the organic matter in the colluvial soils of NW Spain.

Materials and methods

The study area is located on an isolated hill in Campo Lameiro (NW Spain; Figure 1) known as the Paredes section (U.T.M.: X: 538797; Y: 4710597). The area is of great archaeological interest for its petroglyphs (Bradley & Fábregas Valcarce, 1998). In 2002–2004, soil monoliths were taken from local depressions in the hill (alveoli) at 270–320 m above sea level. The soils are depicted in Figure 2, which includes radiocarbon ages of humic acids obtained by the standard acid-alkaline-acid isolation procedure of the Ångstrom Laboratory (Uppsala, Sweden), where accelerator mass spectrometry (AMS) ^{14}C measurements were performed. In this soil type charcoal has a similar age to other forms of organic matter present at the same depth (Kaal *et al.*, 2008b). The monoliths were cut at regular intervals of 5 cm and analysed for C (elemental analysis) and macroscopic charcoal $>$ 2 mm (obtained by wet-sieving of soil samples). The C and macroscopic charcoal contents of the soil layers from

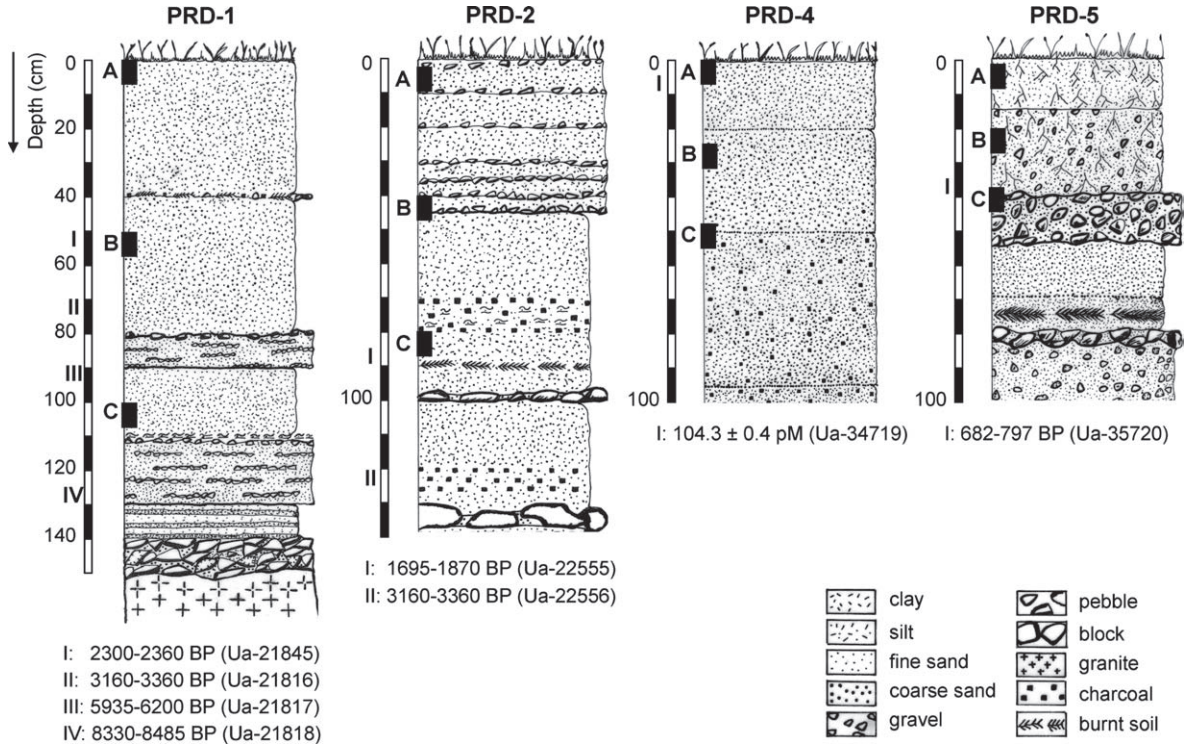

Figure 2 Representation of the soil profiles and the layers that were sampled for thin sections (black rectangles, labelled A–C). Radiocarbon ages are given as 2σ cal ^{14}C year BP or pM (percentage modern) with corresponding codes from the Ångström Laboratory, Uppsala. Drawings are courtesy of M. Costa Casais.

which undisturbed soil samples were collected (see below) are given in Table 1. All C was organic because of the acidic nature of the soils (Kaal *et al*., 2008c). The complex history of soil redistribution in the Paredes section was described by Costa Casais *et al*. (in press).

In March 2006, i.e. before the series of scrubland and forest fires in the summer of that year, three undisturbed soil samples (7 × 5 cm) (Figure 2) were taken from the four profiles at the exact same locations (the scars of the monoliths were still visible). All samples were from colluviated A horizons. Ectorganic layers were not sampled (depth 0 cm is the beginning of the mineral soil). The undisturbed soil samples were air-dried, pretreated with acetone and impregnated with Frencken Synolite (type 544-A-3) polyester resin, using monostyrene as thinner, cyclonox LNC as catalyst and cobaltoctate (1%) as accelerator. After impregnation under vacuum, samples were hardened under a N_2 atmosphere. Consequently, thin sections were prepared according to Jongerius & Heintzberger (1975). The traditional micromorphological classification schemes (e.g. Bullock *et al*., 1985) do not effectively distinguish between charcoal-BC, humified BC and organo-mineral associations of different colour intensity. Also, many other characteristics that can be defined by conventional description of thin sections were not relevant to this study. Therefore, we developed our own simple terminology (Table 2). The 'light' and 'dark' coloured organomineral complexes are mainly organic, as scanning electron microscopy (SEM) showed that only little inorganic material was embedded in them. An example of 'fresh' organic matter is depicted in Figure 3(a,b), 'light' organic matter in Figure 3c and 'dark' organic matter in Figure 3d. Manganese nodules were neither observed in the field nor during sample preparation, and Mn concentration in the soils was very low (85 ± 36 mg kg^{-1}). Therefore, Mn crystals did not interfere with charcoal identification in thin sections.

Using a 6 × 3 cm transparent grid, 18 images were taken at fixed locations of each thin section with a digital camera coupled to a petrographic microscope, at a magnification of 50× under transmitted light. Each image consisted of 8.0×10^6 pixels. The components in the 216 photos were meticulously quantified by means of area calculation (in pixels) with ImageJ open source software of the National Institutes of Health (http://rsb.info.nih.gov/ij/) using the classification of Table 2. Pore space was calculated as the difference between total pixels and the sum of all constituent areas in the images. Percentages of image area were assumed to be equivalent to volumetric contributions. The images cover only 2% of the thin sections (0.7 cm^2), but such analysis is very labour-intensive. All attempts at distinguishing BC from non-BC by automated analysis failed.

Radiocarbon ages showed that the oldest material studied here corresponds to thin section PRD-1C (100–107 cm), which is 6000–8000 cal years old. The other samples are several hundreds up to thousands of years old, except possibly those at the surface of the profiles.

Table 1 Carbon and macroscopic charcoal (> 2 mm) content of the samples used for thin section analysis

	Depth/cm	C/g kg^{-1} soil	Macroscopic charcoal /g kg^{-1} soil
PRD-1A	0–7	91.0	0.64
B	50–57	119.8	0.32
C	100–107	26.6	1.35
PRD-2A	3–10	44.9	0.52
B	40–47	53.4	0.63
C	80–87	87.4	2.22
PRD-4A	0–7	80.5	0.32
B	25–32	38.9	0.96
C	48–55	53.5	3.52
PRD-5A	2–9	63.4	1.17
B	20–27	35.9	0.60
C	37–44	53.0	0.93

Table 2 The classification scheme used for image analysis. OM = organic matter

Constituent	Description
Minerals	Quartz, K-feldspar and mica, i.e. all inorganic matter except for amorphous inorganic material in organo-mineral complexes
'Fresh' OM	Non-charred organic skeleton grains and faecal pellets, sometimes with a recognizable cell structure[a]. See Figure 3(a,b)
'Light' OM	Organo-mineral associations with a yellowish to brown colour and amorphous internal structure[a]. Almost completely organic. See Figure 3c
'Dark' OM	Organo-mineral associations with a deep-brown to black colour and amorphous internal structure[a]. Almost completely organic. See Figure 3d
Black C	Charcoal particles and smaller opaque particles that are clearly distinguished from 'dark' and 'light' OM. See Figure 4
Pore space	All voids, including the intra-pores of charcoals and 'fresh' OM

[a]At a magnification of 50×.

Results and discussion

General properties of thin sections (not related to BC)

Table 3 is a summary of the results of image analysis. The volumetric percentage of pore space was 59 ± 4% (n = 12), which is consistent with the low bulk density of these organic matter-rich soils (Kaal *et al*., 2008c). The voids were mainly compound packing voids between micro-aggregates. The contribution of mineral phases ranged between 8 and 33% (20 ± 9%). The mineral fraction was composed largely of quartz with a smaller abundance of K-feldspar, and some mica was present (3.6 ± 2.0% of total minerals). This is a typical

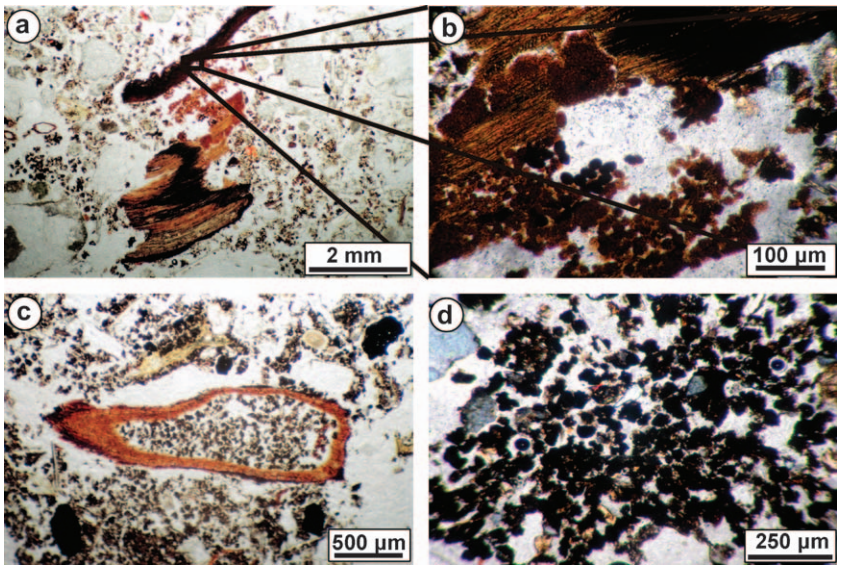

Figure 3 Examples of organic matter forms. (a) 'Fresh' organic matter: a fragment of mainly intact lignified plant material (from PRD-4A). (b) Magnification of the faeces in the same fragment. (c) A fragment of dead plant material with largely intact ligneous outer walls and the aggregated faeces (i.e. 'light' organic matter) of its interior (PRD-1A). (d) 'Dark' organic matter in micro-aggregates (PRD-2C).

mineralogical fingerprint of weathered granite. The volumetric contribution of all forms of organic matter, including BC, ranged between l2 and 31% (21 ± 6%). Organic matter content as estimated by image analysis and C content of the fine earth fraction were statistically related ($n = 12$; $r = 0.80$, $P = 0.002$).

The only thin section containing significant amounts of root fragments with intact cortical tissue, faeces of decomposer organisms (mostly mite excreta) and possibly partially degraded leaves was section PRD-4A (Figure 3a,b). The presence of faeces in the majority of the root fragments in PRD-4A suggests recent faunal activity: these excrements were scarce or absent in the remains of root fragments in the surfaces of the other soils. This result is in concordance with Kaal *et al.* (2008c), who inferred that the surfaces of all profiles except for that of PRD-4 are old erosion surfaces, containing only small amounts of undecomposed organic matter.

Table 3 Results of image analysis. Values indicate volumetric percentages, with standard deviations between parentheses ($n = 18$ images)

	Depth /cm	Minerals /%	Organic matter /%	Pore space /%
PRD-1A	0–7	11 (9)	31 (12)	58 (12)
B	50–57	8 (9)	30 (8)	63 (8)
C	100–107	31 (13)	12 (5)	57 (12)
PRD-2A	3–10	22 (15)	19 (7)	60 (14)
B	40–47	9 (9)	24 (7)	66 (11)
C	80–87	11 (10)	27 (13)	62 (16)
PRD-4A	0–7	20 (16)	16 (7)	64 (14)
B	25–32	24 (16)	16 (6)	60 (15)
C	48–55	29 (21)	17 (7)	54 (19)
PRD-5A	2–9	25 (14)	22 (5)	53 (14)
B	20–27	33 (12)	13 (5)	53 (11)
C	37–44	18 (11)	21 (8)	60 (13)

The presence of micro-aggregates in the interior of a degraded fragment of lignified tissue (Figure 3c) in PRD-1A suggests that they were derived from the coalescence and transformation of faeces (Buurman & Jongmans, 2005). The similarities between the micro-aggregates within the structure and the matrix outside of it suggest that they have a common origin. van Mourik (1985) showed that a large fraction of the organic matter in Atlantic rankers consisted of 'welded modexi' (deformed and aggregated faecal pellets). Accordingly, the 'light' micro-aggregates are probably derived from excremental fabric. Finally, some samples contained large and dense organo-mineral aggregates, most of which included quartz grains. The origin of these so-called glaebules in the soils studied is unclear.

Black carbon

The problem of distinguishing charcoal from non-charred organic matter is illustrated by Figure 4. Although many of the larger charcoal fragments were obviously degraded, they often contrasted strongly with the surrounding matrix (Figure 4a–c). When a charcoal fragment was embedded in a light-coloured organo-mineral matrix (Figure 4d), it could also be reliably identified. Identification of BC particles that occurred in a dark-coloured organo-mineral environment (Figure 4e), however, was more difficult. In particular, particles having a deep black colour and well-defined edges that occurred in large and relatively dense organo-mineral glaebules (Figure 4f) could not be labelled as BC with certainty. Therefore, in estimates of volumetric BC content, only the completely opaque particles with smooth rounded to subangular structure, sharp boundaries, and sometimes clear open lumina (of vessels) were classified as BC in the present paper.

The volumetric contributions of the organic matter fractions obtained by analysis of the 216 images are given in Figure 5.

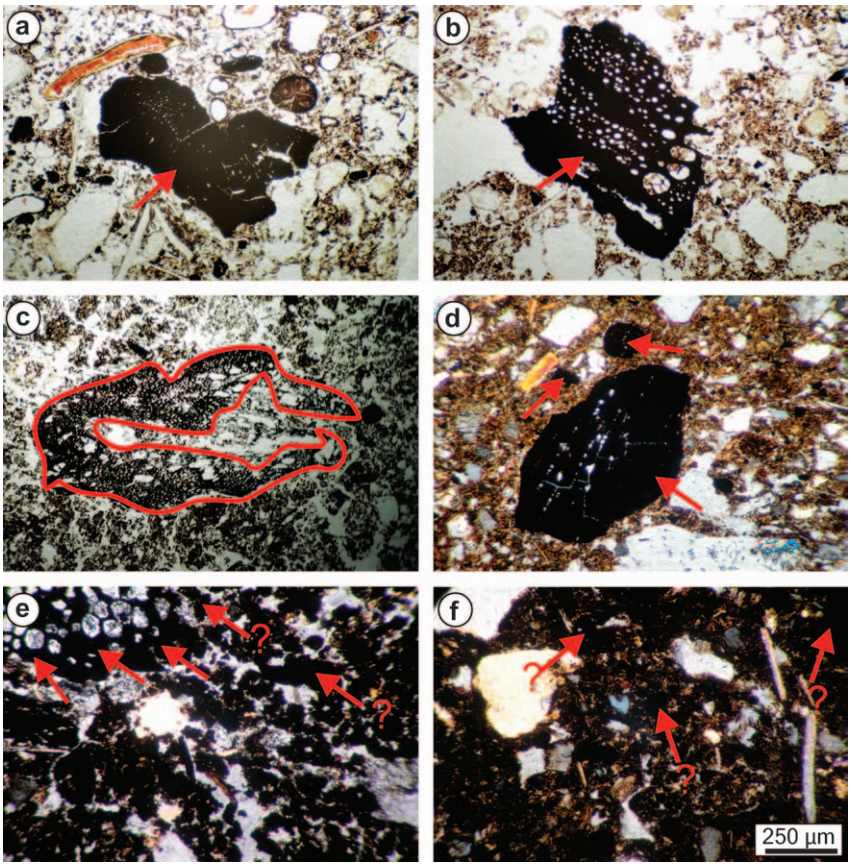

Figure 4 Black C in different matrices. (a–b) Charcoal and un-decomposed ('fresh'; see Table 2) organic matter in a matrix of minerals and 'light' organic matter (4a from PRD-5B, 4b from PRD-1C). (c) A strongly degraded charcoal fragment (bordered) in 'dark' organic matrix from section PRD-1B. (d) Charcoal fragments in a 'light' organomineral matrix (PRD-4B). (e) Black C in dark microgranular matrix (PRD-1B). (f) Potential BC in a glaebule (PRD-2C). The scale bar in the lower right corner applies to all images.

Volumetric BC content ranged between 10 and 60% (on average 26%) of the organic matter. The largest BC content was obtained for PRD-2C, which was directly below a charcoal layer. Macroscopic charcoal (> 2 mm) content determined after wet sieving was not related to the estimated BC content from image analysis. Pyrolysis-GC/MS already showed that macroscopic charcoal concentration was not related to the concentration of pyrolysis markers of BC markers (Kaal *et al*., 2008a), suggesting that macroscopic charcoal represents the incomplete combustion of bulky wood material that is not necessarily proportional to the total amount of BC in a given sample. However, because only limited areas of images were analysed, and semi-quantitative methods were applied, this explanation is tentative. Quantitative comparison of volumetric BC contributions with any other method would require the unambiguous differentiation between the charred and non-charred elements of the 'dark' organic matter.

As mentioned earlier, the 'fresh' and 'light' organic fractions were not BC. The 'dark' organic matter was partially deep black and therefore potentially BC-derived. Such material might have formed by 'melanization' (the process of dark colouring by accumulation of very dark to opaque organic matter). An example of melanized organic material by van Mourik (1985) has characteristics of charcoal (deep black, sharp boundaries). We hypothesize that BC can play the role of the melanization agent in Atlantic rankers, giving the soils a blackish appearance. The 'dark' organic fraction would then be a mixture of degraded organic matter in the form of aggregated faeces and unknown quantities of BC. This would imply that the proportions of BC given in Figure 5 were under-estimates of actual volumetric BC content.

We found numerous charcoal particles that were severely degraded. The biological attack on charcoal is illustrated by the arthropod excreta in the SEM micrographs of a weakly charred wood fragment from PRD-4A (Figure 6). One of the main goals of BC research is to estimate its role in C cycling: BC degradation products should therefore be included in global BC estimates until they are mineralized. It is reasonable to assume that, with further degradation, the BC will eventually become morphologically unrecognizable because of mixing with inorganic material and non-BC organic matter. Likewise, Bertran *et al*. (1991) not only found charcoal in their thin sections from Atlantic rankers in north Portugal, but also frequent 'humified organic fragments of black colour'. Thus, as well as easily recognizable charcoal particles, additional pyrogenic C may have been present as apparently amorphous material (Glaser *et al*., 2000; Schmidt *et al*., 2002; Brodowski *et al*., 2005; Cohen-Ofri *et al*., 2006).

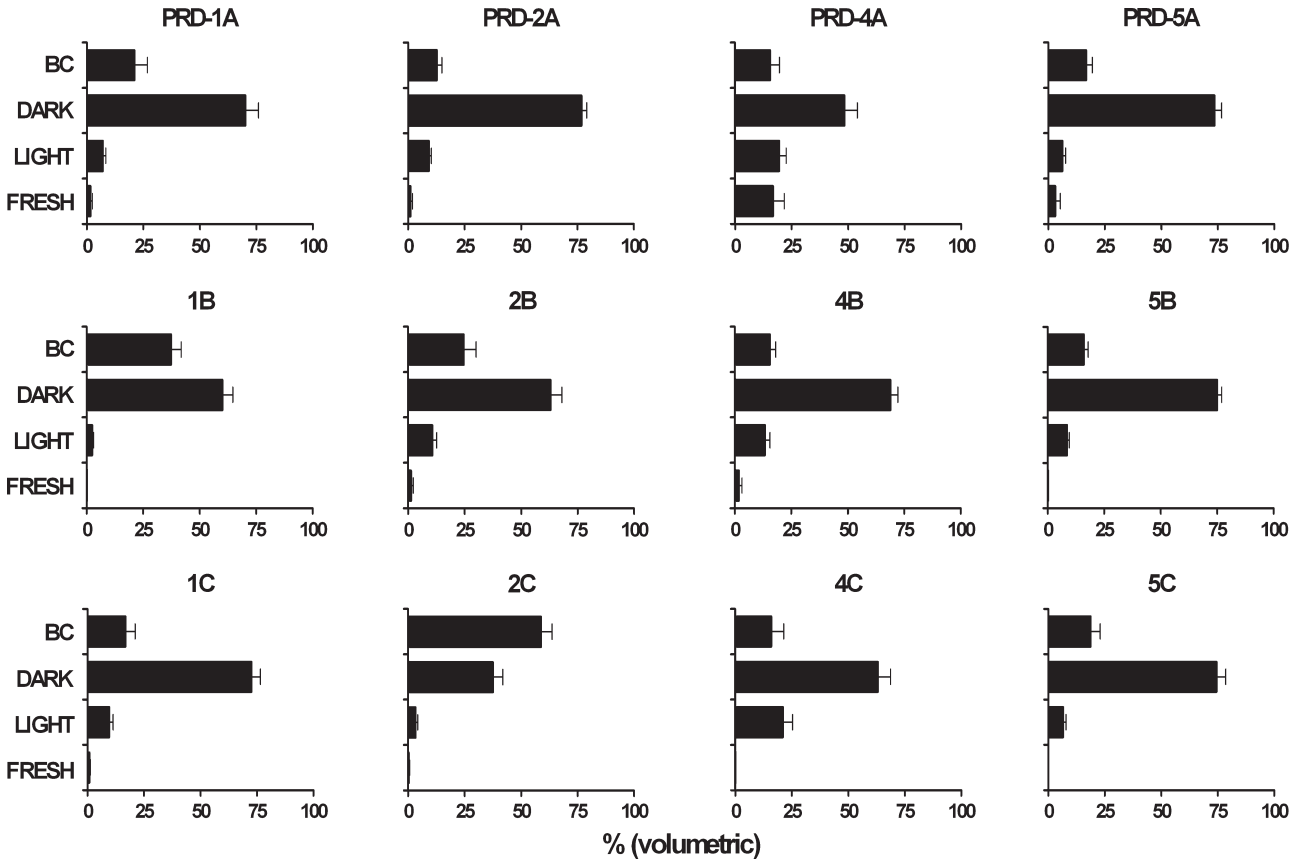

Figure 5 Volumetric proportions of organic matter forms (see Table 2) as obtained by image analysis. BC = black C. Error bars represent the standard error of the mean ($n = 18$ photos).

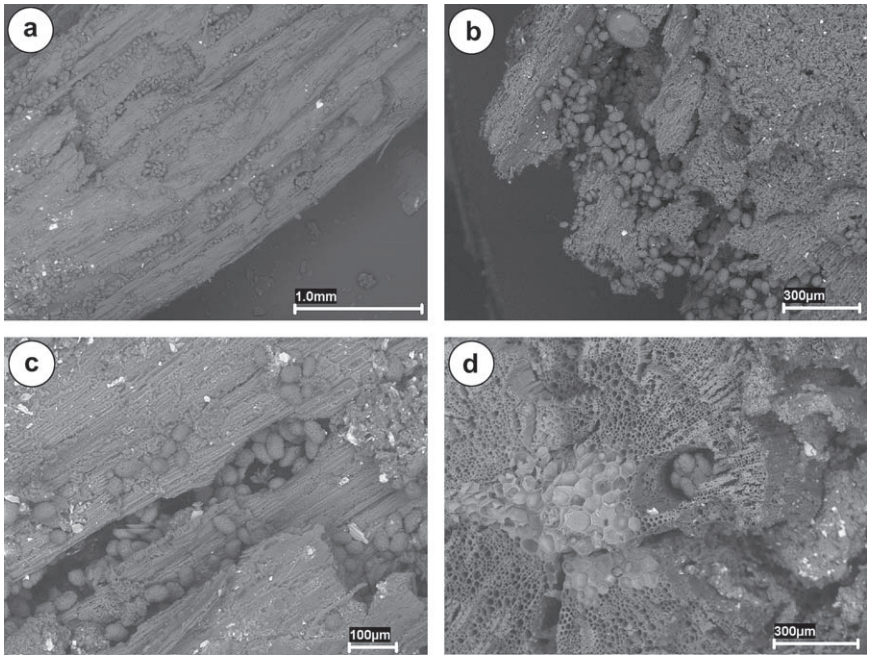

Figure 6 SEM micrographs of a charcoal fragment from PRD-4A under xylophagous attack. (a–c) Longitudinal orientation, (d) transverse section showing a xylophage chamber next to carbonized pith.

Recapitulating, some intact plant remains and faecal pellets were present ('fresh' organic matter), but the vast majority of the organic matter was (biologically) degraded ('light' and 'dark' organic matter) or charred (BC and an unknown fraction of 'dark' organic matter). A large proportion of the non-charred organic matter had coalesced into micro-aggregates. This organic matter may have been protected against decomposition through sorption/complexation of reactive Al (Carballas *et al*., 1979; Schwesig *et al*., 2003) and/or through inclusion within micro-aggregates (Six *et al*., 2004; Nierop *et al*., 2005; Buurman *et al*., 2007). Black C was present in micromorphologically recognizable structures, but was in all likelihood also in the 'dark' organic matter. Thus, BC may have resisted decomposition because of its chemical recalcitrance (Krull *et al*., 2003), but also through sorptive and complexation interactions (Czimczik & Masiello, 2007) and occlusion in micro-aggregates (Brodowski *et al*., 2006). It seems likely that the longevity of the BC in the soils studied can be ascribed to a combination of these stabilization mechanisms.

The unequivocal yet qualitative evidence of significant BC contribution to the organic matter in combination with the evidence obtained by molecular characterization techniques (Kaal *et al*., 2008a) allows us to postulate that the abundance of BC in Galician colluvial soils (Atlantic rankers) has been severely under-estimated. Analysis of thin sections is a useful tool when the presence of BC in complex and aged soil organic matter mixtures is to be ascertained.

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MANUSCRIPT 6

Characterisation of aged charcoal using a coil probe pyrolysis-GC/MS method optimised for black carbon.

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Characterisation of aged charcoal using a coil probe pyrolysis-GC/MS method optimised for black carbon

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ABSTRACT

Molecular identification of aged black carbon (BC) is problematic owing to potential interference of non-charred aromatic organic matter and to a general lack of techniques that are capable of providing detailed chemistry of it. Pyrolysis-GC/MS is thought to be unsuitable for analysis of BC because the pyrolysis step itself causes molecular rearrangements that may interfere with the thermal modifications by natural burning, and because a significant fraction of BC is not pyrolysable.

We optimised a coil probe pyrolysis method for BC by analysing both a lignin-rich peat sample and an aged legume-derived charcoal at various temperatures (400–1200 °C). Pyrolysis at 750 °C for 10 s combined acceptable thermal modifications to the pyrolysed peat with high-quality chromatograms from charcoal.

Using this method we analysed 91 samples of up to >11,000 yrs old oak, birch and legume charcoal from a colluvial soil in NW Spain. The charcoal produced a large suite of aromatic compounds that can be considered characteristic of BC in this study: benzene, toluene, PAHs (naphthalene, biphenyl, fluorene and phenanthrene) and N- and O-containing (poly)aromatics (e.g. dibenzofuran and benzonitrile). A series of N-containing compounds that had not been previously reported in charcoal pyrolysates were found (C_1-benzoxazole, benzene dicarbonitriles, 2-phenylpyridine, naphthalenecarbonitrile, 2-biphenylcarbonitrile). Small amounts of short-chain *n*-alkane/*n*-alkene pairs indicated some aliphatic material had survived the fire. Uncharred or weakly charred carbohydrate substances in the charcoal were identified as levoglucosan, levoglucosenone, furans and furaldehydes.

Charcoal fragments from different plants produced similar pyrolysates. Markers of 'thermolabile' (non-charred or weakly charred) biomass disappeared as sample age increased. Nonetheless, signal intensity improved with age, suggesting that the pyrolysability of the relatively 'thermostable' (condensed) BC fraction increased. We postulate that gradual oxidation of the condensed aromatic backbone of BC enhanced its susceptibility to pyrolysis.

1. Introduction

Charred solid organic residues produced during biomass burning are collectively referred to as black carbon (BC). Depending on the extent of thermal alteration (C enrichment, aromatisation, condensation of aromatics), BC can take any form along the continuum of weakly charred plant material through charcoal to soot [1,2]. While soot is a highly condensed aromatic network formed during recondensation of reactive gases within flames, weakly charred biomass may retain most of the morphological and chemical properties of the fuel [3]. Although the average level of thermal impact on charcoal-BC is somewhere in between that of weakly charred biomass and soot, a charcoal particle can be a heterogeneous mixture of weakly-to-severely aromatised biomass, trapped combustion products and tar, sometimes comprising an uncharred interior [3,4].

Recent studies have shown that BC is not as 'inert' in the environment as previously thought. Post-fire surface oxidation further increases the chemical heterogeneity of BC [5–7]. Through oxidation, BC may become extractable in aqueous solutions, allowing it to interfere in humic substances extracts [8–10] and leach out of a soil [11,12]. However, these and other BC 'loss' processes are not profoundly understood, and their effects on different BC types or in different soil types are virtually unknown [3]. This knowledge is urgently needed because (1) BC may have a significant contribution to recalcitrant organic matter and consequently play an important role in global C cycling [13,14], (2) BC immobilises highly toxic organic compounds [15], (3) BC controls

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soil formation processes [16,17] and (4) BC is increasingly implemented into agricultural systems for improving soil fertility and crop production, reducing land degradation and cutting net greenhouse gas emissions [18–20].

Elucidating the fate of BC is aggravated by the lack of a standardised method for identifying and quantifying it [21,22]. Applying various common methodologies to quantify the content of BC in soils to a diverse set of BC reference materials, Hammes et al. [23] concluded that each method assesses different fractions of the BC continuum and that the methods are not systematically related. In addition, most BC characterisation studies are concerned with recent natural or laboratory-produced BC, while the degradation products of BC in soils and sediments may have a different composition and require different approaches [24]. Novel advanced methodologies which may provide quantification or characterisation of BC but are so far seldom employed are improved benzene polycarboxylic acid analysis (BPCA method [25]), thermogravimetry–differential scanning calorimetry–isotope ratio mass spectrometry (TG–DSC–IRMS [26]), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy [5]) and ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with electrospray ionisation [10,12].

Analytical pyrolysis is a less modern technique that uses controlled invasive thermal degradation to break down large molecules for identification [27]. The resultant pyrolysis products (the pyrolysate) are commonly separated and identified using gas chromatography and mass spectrometry, hence pyrolysis-GC/MS. In general, the method does not require solvents or pre-concentration of the sample and is not excessively time consuming. Pyrolysis-GC/MS has a pivotal role in the characterisation of soil and sedimentary organic matter, but great care must be taken during interpretation of any pyrolysate because many biocomponents may lose diagnostic chemical groups during pyrolysis and secondary rearrangements of reactive intermediates produce structures that did not occur in the original macromolecule [27,28]. Proteins for instance may lose N-containing functional groups; polysaccharides release H_2O thereby producing levosugars or furans and pyrans by more drastic dehydration; fatty acids may decarboxylate producing *n*-alkane/*n*-alkene pairs of which a small proportion may cyclisise to alkylbenzenes and alkylnaphthalenes and small radicals may recombine forming a wide array of compounds [28–31]. Fortunately, the presence of one given pyrolysis product may help to identify the origin of another. For instance, if furans are much less abundant than levosugars, the most likely source of both is intact polysaccharides, while furans that are not accompanied by levosugars are more likely derived from biodegraded or slightly charred polysaccharides. Also, alkylnaphthalenes may form upon cyclisation of fatty acids, but if aliphatic pyrolysis products are negligible a BC origin is likelier. Finally, proteins produce a wide and variable array of N-containing pyrolysis products, but if benzonitriles and quinolines are the most abundant ones, the protein may well have been subjected to thermal modifications [4,32]. Therefore, careful examination of the whole set of pyrolysis products allows us to allocate many of them to a specific biocomponent class and establish the degradation state in which it occurred.

Despite the analytical drawbacks of pyrolysis-GC/MS, various authors attempted to provide information on BC composition by pyrolysis-GC/MS. Pastorova et al. [33] and Boon et al. [34] successfully applied pyrolysis-GC/MS to investigate the effect of laboratory charring on cellulose. Untreated cellulose produced mainly 1,6-anhydro-β-D-glucopyranose (levoglucosan), which was substituted by furans and later also PAHs with increasing pre-pyrolytic thermal modifications. Naafs [35], Ross et al. [36] and Rumpel et al. [37] used PAHs as tracers of BC in complex organic matrices. Knicker et al. [38] used pyrolysis-GC/MS to identify uncharred lignin material in charred plant residues obtained from a fire-affected soil in Southern Spain. Specific pyrolysis products of BC were not observed in that study. De la Rosa [4] reported the pyrolysis-GC/MS signatures of various types of BC reference materials. These reference materials produced predominantly benzene, toluene, *p*-xylene and naphthalenes upon pyrolysis. While these products may form upon many precursors other than BC (e.g. polysaccharide, protein, lignin, lipid), when they are not accompanied by the markers of their precursors (levoglucosan, furans, pyrroles, methoxyphenols, *n*-alkanes/alkenes, etc.), a BC origin is more likely.

Apart from the thermal modifications induced by pyrolysis, another problem emerges when applying pyrolysis-GC/MS to BC. The signal intensity of pyrograms obtained from BC is generally lower than that of non-charred biomass, which is a consequence of the presence of polycondensed aromatics with strong C–C bonds, stable under pyrolysis conditions. This fraction is referred to as non-pyrolysable material [4,29,37–42]. Pyrolysis-GC/MS is, however, a valuable tool to identify the 'thermolabile' fraction of BC [43]. In pyrolysis-GC/MS it is paramount to select a temperature at which the pyrolysed material is representative of the sample and at which a macromolecule is degraded to a wide array of GC amenable products [27]. With increasing temperature, more bonds will be broken but the pyrolysate will consist of smaller and less characteristic fragments [44]. Additional difficulties in distinguishing the two steps of thermal modifications involved (natural fire and artificial pyrolysis during analysis) may thus be anticipated [45,46]. Nonetheless, increasing the pyrolysis temperature augments the proportion of BC reaching the MS, and if the severity of secondary rearrangements can be estimated, information on the chemical structure of BC may be revealed.

A previous study showed that Curie-point pyrolysis-GC/MS at 600 °C of NaOH-extractable soil organic matter from a colluvial soil in Campo Lameiro (NW Spain) produced large amounts of most likely BC-derived pyrolysis products (benzene, toluene, PAHs and benzonitrile) [32]. This observation was confirmed by the omnipresence of charcoal (as obtained by wet sieving), high concentrations of charred material (from ^{13}C DP NMR spectra interpreted using a molecular mixing model), presence of benzene polycarboxylic acids (from Thermally assisted Hydrolysis and Methylation (THM)), production of benzene polycarboxylic acids in the BPCA method [25] and conspicuous BC and finely divided BC-like structures in thin sections (micromorphological examination) [47,48]. It was suggested that BC becomes increasingly amenable to pyrolysis-GC/MS during long-term storage in soil [47].

In this work, we optimise pyrolysis-GC/MS for charcoal-BC using peat and charcoal in order to: (1) determine the molecular composition of charcoal from another colluvial soil in Campo Lameiro, (2) study the influence of age (recent to >11,000 cal yrs) and plant type (oak, birch, legume) on charcoal's pyrolysis fingerprint and (3) test the hypothesis that BC becomes increasingly amenable to pyrolysis-GC/MS with time and increasing pyrolysis temperature.

2. Experimental

2.1. Study site

The study area is located in Campo Lameiro (NW Spain; U.T.M.: X: 538797; Y: 4710597). The site is on an isolated hill (Monte Paradela) at ~300 m above sea level, 25 km east from the Atlantic Ocean. The parent rock is migmatitic granite. The soil (Haplic Umbrisol (humic/alumic) [49]) was traditionally referred to as 'Atlantic ranker' and is characterised by a high content of organic

matter that is thought to have resisted biodegradation through sorptive protection by poorly-crystalline Al phases [50]. However, the presence of BC may be a complementary cause for the slow decomposition of organic matter [51].

The soil studied here is a 2.35 m deep colluvium known as PRD-4. A soil monolith was cut from an archaeological trench and sliced into 5 cm sections producing 47 samples. Accelerated mass spectrometry ^{14}C ages of the soil organic matter obtained by a standard acid–alkaline–acid extraction procedure were performed by Beta Analytical Inc. (Miami, USA) and the Ångstrom Laboratory (Uppsala, Sweden). The sample at 190–195 cm depth gave a ^{14}C age of 11,240–11,130 cal BP (2σ; laboratory code Beta-240963) and the sample between 5 and 10 cm depth 104 pM (percentage modern, laboratory code Ua-34179), indicating that the soil sequence covers the entire Holocene. The age of other samples was estimated as described in [52]. In that paper we also explain why the ^{14}C measurements may be used for estimating the age of the charcoal from the dated samples.

Macroscopic charcoal (>2 mm) was isolated by wet sieving. All 47 samples yielded charcoal, rendering this soil a unique opportunity for studying the Holocene evolution of wood-derived charcoal-BC. The anatomical properties of the charcoal were determined under a reflected light microscope, which allowed for the botanical identification of 840 charcoal fragments (this type of charcoal analysis is known as anthracology [53]). The vast majority of the charcoal derived from oak (*Quercus* sp., 61%), legumes (Fabaceae, 21%), birch (*Betula* sp., 6%) and heather (*Erica* sp., 6%). A representation of the soil profile and macroscopic charcoal content can be found in [54]. Of each sample, 2–4 fragments were ground and analysed by pyrolysis-GC/MS.

Additionally, a *ca*. 6200 yrs old Fabaceae-derived charcoal collection from soil PRD-2 in Campo Lameiro and a dried and ground *ca*. 1800 yrs old sample from the ombrotrophic peat bog *Pena da Cadela*, also from NW Spain [55,56], were used for optimisation of the pyrolysis-GC/MS method. The peat sample consisted of carbohydrate and lignin-rich peat in the hemic state of decomposition. We assume that by monitoring the secondary pyrolysis rearrangements of the peat sample (e.g. formation of PAHs from lignin and carbohydrates) we can estimate the repercussions of pyrolysis rearrangements to non-charred material in the charcoal as well.

2.2. Pyrolysis-GC/MS

Platinum filament coil probe pyrolysis-GC/MS was performed with a Pyroprobe 5000 (Chemical Data Systems, Oxford, USA) coupled to a 6890N GC and 5975B MSD GC/MS system from Agilent Technologies (Palo Alto, USA). In comparison with the other widely used type, i.e. Curie-point pyrolysis, coil probe pyrolysis systems have the advantage that high temperatures (>1000 °C) can be achieved, that the quartz tubes used have a large sample capacity and that variable temperature experiments can be performed. On the other hand, the quartz tubes shield off some of the heat applied to the coil probe from the sample, so that the actual heat applied to the sample cannot be constrained [57,58]. Samples (1–1.5 mg) were embedded in glass wool-containing fire-polished quartz tubes. A methylstyrene-based contamination was removed from the wool by repetitive heating at 1200 °C in the pyrolysis chamber. The charcoal and peat samples (see above) were pyrolysed at temperatures ranging between 400 and 1200 °C for 10 s (heating rate 10 °C/ms). The non-pyrolysable residue was re-analysed by pyrolysis at 1000 °C in some cases (see Section 3). Samples were pyrolysed shortly after insertion in the probe's interface to minimise thermal desorption and degradation prior to pyrolysis. The interface and GC inlet were set at 250 °C. A rapid GC cycling program was required given the number of samples studied: the oven was heated from 40 to 100 °C at 8 °C/min and then to 250 °C at 20 °C/min and held isothermal for 5 min. Preliminary experiments showed that increasing the maximum temperature of the GC oven to 300 °C did not result in the elution of any significant and comprehensible pyrolysis products, but cold-trapping of some high molecular weight pyrolysis products (for instance in the pyrolysis interface) cannot be discarded [58]. The GC/MS transfer line was held at 270 °C, the ion source (electron impact mode, 70 eV) at 230 °C and the quadrupole detector at 150 °C. The GC used was equipped with a (non-polar) HP-5MS 5% phenyl, 95% dimethylpolysiloxane column (length 30 m; internal diameter 0.25 mm; film thickness 0.25 μm). Helium was used as the carrier gas (constant gas flow, 1 ml/min). Compounds were identified using the NIST '05 library and pyrolysis-GC/MS literature [35,45,59–61].

Each pyrolysis product has a different response factor by the MS. This does not inhibit a reliable comparison between samples but it does mean that the results are not absolutely quantitative.

3. Results and discussion

3.1. Peat and charcoal: variable pyrolysis temperature experiments (400–1200 °C)

Total ion chromatograms (TICs) of the peat and charcoal samples used for method optimisation are presented in Fig. 1. Peak numbers in that figure refer to the compounds depicted in Fig. 2.

Pyrolysis/thermal desorption at 400 °C of the peat sample (Fig. 1) produced mainly levoglucosan and a series of methoxyphenols (guaiacols and syringols), which are typical pyrolysis products of cellulose and lignin, respectively [62]. Most abundant lignin markers were 4-vinylphenol and 4-vinylguaiacol, which are the decarboxylation products of *p*-coumaric acid and ferulic acid, respectively [63,64], and are typical pyrolysis products of lignin from grasses [65,66]. Aliphatic pyrolysis products from lipids (primarily *n*-alkane/*n*-alkene doublets) were scarce and the products of tannins such as catechol and pyrogallol were negligible. Virtually all identified aromatics derived from lignin, except for perhaps phenol and C_1-phenols that may also derive from e.g. carbohydrate and proteinaceous precursors [67]. This pyrolysate represents a relatively 'thermolabile' fraction of the peat: the ether linkages between lignin monomers and particularly the glycosidic bonds of cellulose are easily pyrolytically cleaved [29]. Pyrolysis at 500 °C produced an additional series of straight-chain aliphatics (dominated by alkenes) while the contribution of levoglucosan and levoglucosenone decreased. These differences were probably the effect of some structural rearrangement of cellulose at 500 °C but, more importantly, of a more complete pyrolysis of aliphatics and lignin. This conclusion was drawn from the following observations: (1) ^{13}C CPMAS NMR showed that the proportions of carbohydrate and lipids were similar (unpublished results), suggesting that the aliphatic fraction was severely underrepresented in the 400 °C pyrolysate, (2) although the TIC is not a reliable quantitative measure, a marked 2.5-fold increase from 400 to 500 °C suggested more complete pyrolysis at 500 °C (Fig. 1) and (3) structural rearrangement of the polysaccharide would produce a relative increase in the contributions of furans and furfurals, which was not observed [33]. For the same reasons, the contribution of aliphatics (and TIC) increased further at pyrolysis temperatures reaching 600–800 °C and the contribution of phenols increased because of partial demethoxylation of the guaiacol and syringol moieties of lignin [38,40]. Furthermore, the contribution of benzene, toluene and naphthalene increased, indicating further loss of phenolic functional groups and carbohydrate rearrangement. Finally, after pyrolysis/gasification temperatures of 1000 and 1200 °C, benzene, toluene and aliphatics

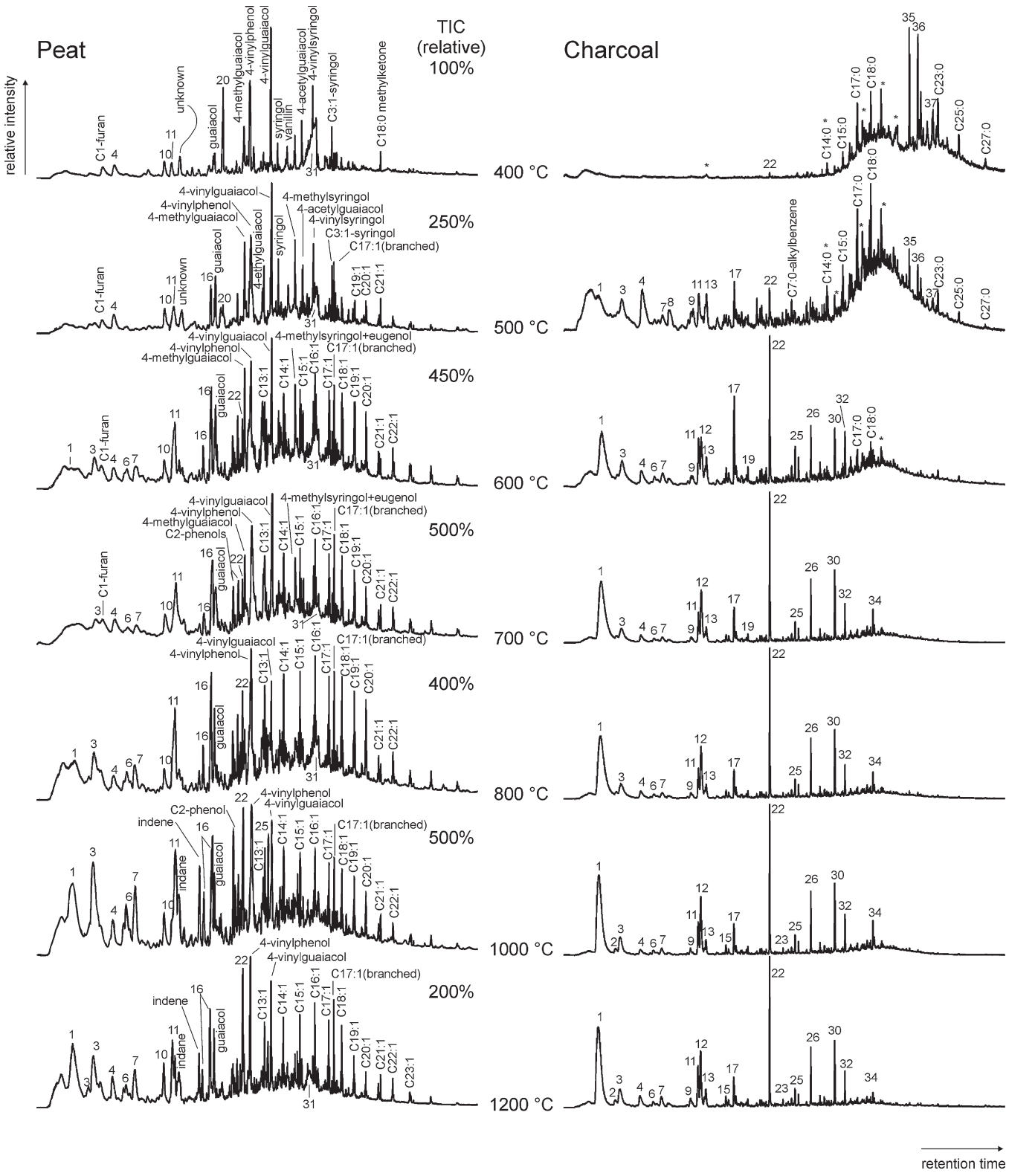

Fig. 1. Total ion chromatograms of peat and charcoal analysed at different pyrolysis temperatures. Numbers refer to pyrolysis products depicted in Fig. 2. C*n*:0 = alkane with chain length *n*; C*n*:1 = *n*-alkene. * = contamination. TIC = total ion current (signal intensity).

dominated the chromatograms and also peaks of phenol and naphthalene were recorded, while levoglucosan diminished and the signal of carbohydrate-derived furans increased. These results confirmed earlier studies that (1) lignins decarboxylate, demethoxylate and eventually dehydroxylate with increasing degree of charring [42], (2) polysaccharide rearrangements produce principally furans and probably naphthalene at higher temperatures [33,34], (3) the precursors of the aliphatic pyrolysis products are relatively resistant to thermal modifications [68] and (4) heating causes an overall increase in aromaticity [69]. These changes in pyrolysate composition clearly illustrate progressive artificial charring with increasing pyrolysis temperatures. When

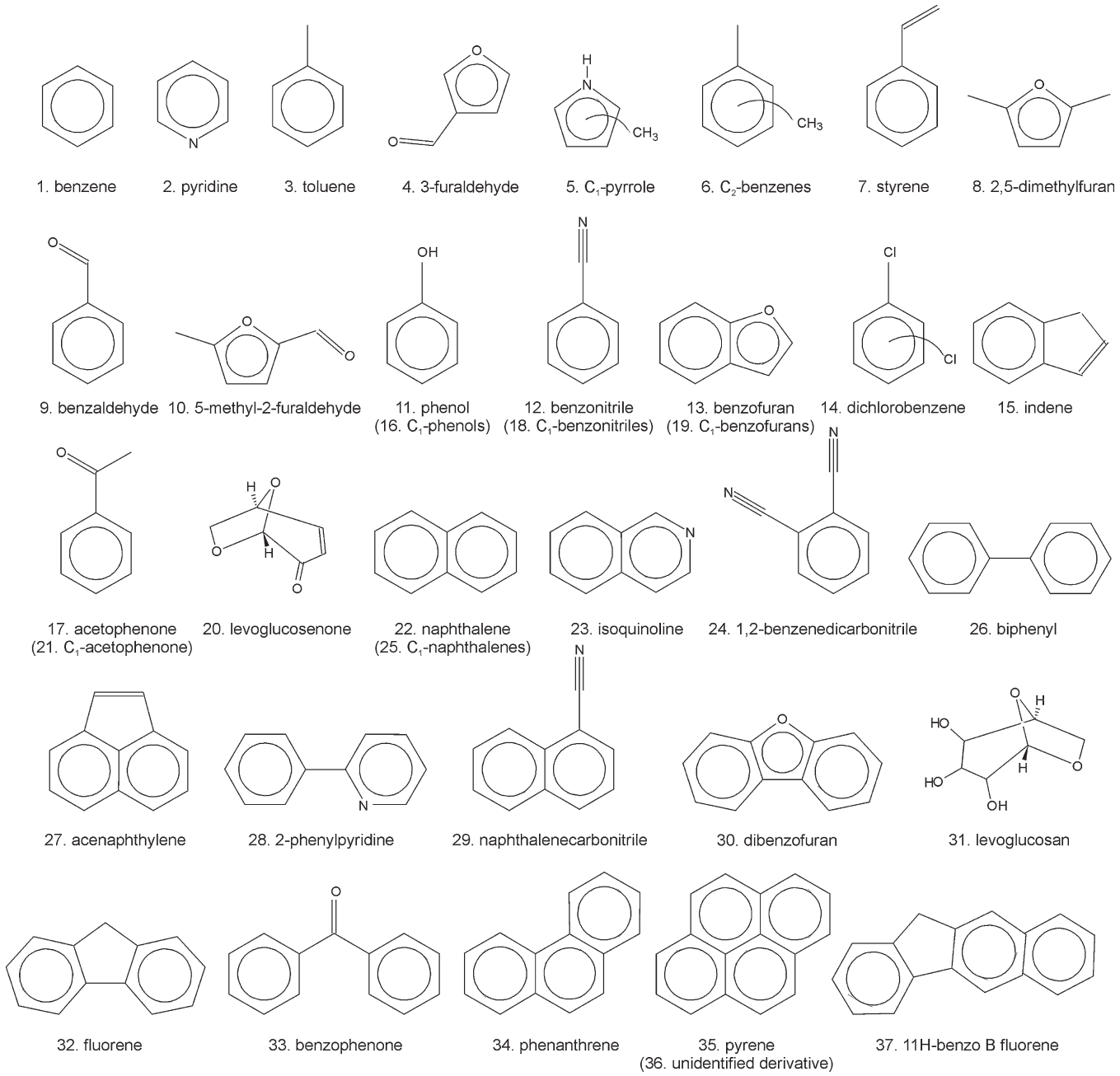

Fig. 2. Selection of pyrolysis products observed in charcoal. Compound numbers correspond to the peaks in the spectra of Figs. 1, 4 and 5.

applied at 600–800 °C, pyrolysis-GC/MS produced predominantly lignin, carbohydrate and lipid markers (mainly 4-vinylphenol, guaiacols, syringols, levoglucosan and aliphatics), while only small peaks were observed for the products of charred material produced in the pyrolysis head (benzene, toluene and naphthalene).

As expected, completely different pyrolysis fingerprints emerged from *ca.* 6200 yrs old legume charcoal from soil PRD-2 analysed under the same conditions (Fig. 1). At 400 °C, the spectra were dominated by a weak signal of aliphatics and silicon–rubber probe seal and column bleed contaminations (Fig. 1), indicative of insignificant bond cleavage of the material. Furthermore, some pyrene and other PAHs were observed, probably reflecting volatile BC structures rather than cleaved polyaromatics. The signal of the pyrogram obtained by pyrolysis at 500 °C was also of poor quality, although the diversity of products in the short retention time domain increased markedly, which means that some material was indeed pyrolysed at this temperature. Peaks of benzene, toluene, phenol, benzofuran, acetophenone and naphthalene represented a thermolabile fraction of BC, probably with some uncharred or weakly charred components (reflected by 3/2-furaldehyde and 2,5-dimethylfuran). Levosugars were not present, indicating that unaltered polysaccharides were negligible [70]. At 600 °C, relatively large amounts of benzene, toluene, benzonitrile, naphthalene, biphenyl, dibenzofuran and fluorene were measured, all of which are known products of BC [4]. Thus, the contribution of BC products increased by comparison to carbohydrate and lipid markers, which was indicative of a larger fraction of pyrolysable BC. The pyrolysates were similar for the charcoal pyrolysed in the 700–1200 °C range, although the contribution of aliphatic products declined progressively towards the high temperature end. The general trend with increasing pyrolysis temperature (mainly occurring between 500 and 700 °C) is a relative decrease in

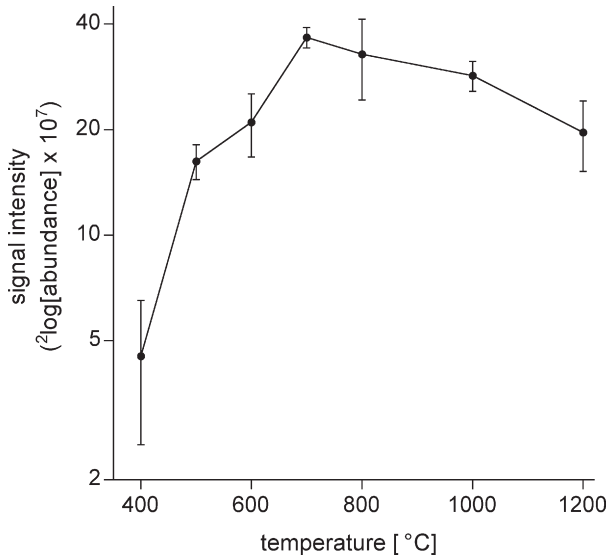

Fig. 3. Pyrolysis temperature plotted against signal intensity for charcoal. Error bars indicate standard error of the mean (two replicates).

aliphatic and thermolabile precursors and increasing contributions of BC-derived pyrolysis products. It is very unlikely that this trend mirrored artificial charring alone, because (1) only weak artificial charring of the peat sample at 500–700 °C was observed and the aliphatics did not seem to be subjected to significant aromatisation, and (2) the increase in signal intensity with temperature (Fig. 3) suggests a much less complete pyrolysis of the sample below 600 °C than above. Moreover, charcoal is obviously more likely to consist of aromatics than of a series of aliphatics and carbohydrates. It is safe to conclude that pyrolysis of charcoal-BC was more efficient at higher temperatures.

The charcoal was best characterised by pyrolysis at 700 °C and higher. Because peat-derived lignin lost some of its characteristics at 800 °C and higher, a pyrolysis temperature of 750 °C was expected to combine good quality chromatograms with limited structural rearrangements in the pyrolysis chamber.

The 750 °C pyrolysis method was tested on the oak and legume-derived charcoal fragments of the same 6200 yrs old sample (Fig. 4). Independent of charcoal species, chromatograms were dominated by benzene with additional peaks from a wide array of other 1-ring homocyclic aromatics (toluene, C_2-benzenes, styrene, benzaldehyde, acetophenone, phenols, benzonitrile), PAHs (e.g. naphthalenes, biphenyl, fluorene, naphthalene carbonitrile, phenanthrene, pyrene), O-substituted heterocyclic aromatics (3/2-furaldehyde, benzofuran, dibenzofuran) and N-substituted heteroaromatics (C_1-pyrrole, pyridine, indole, (iso)quinoline, phenylpyridine). The residue in the quartz tube was re-pyrolysed at 1000 °C. The pyrolysate of this 'second shot' was dominated by benzene, benzonitrile, naphthalene, biphenyl, dibenzofuran and fluorene (Fig. 4). This relatively thermostable residue thus consisted of a condensed aromatic network containing significant amounts of N (recognised as benzonitrile). Replicates produced similar results (Fig. 4). Twenty other charcoal fragments of *inter alia Clematis* sp., *Arbutus unedo* and *Erica arborea* were analysed (not shown). The differences in pyrolysate composition between species of the same age were very small, which suggests that bond scission and also secondary reactions are highly reproducible, and that the pyrolysis of BC proceeds by consistent but yet unknown laws. The chromatograms obtained from younger charcoal were markedly different from those obtained from the older charcoal. Therefore we shifted to the soil profile with the longest time range, PRD-4, which is the subject of the remainder of this paper. For this soil, we analysed charcoal from oak, birch and legumes.

3.2. High resolution pyrolysis-GC/MS record of PRD-4 charcoal

A total of 91 charcoal samples from soil PRD-4 were analysed by pyrolysis at 750 °C for 10 s. The pyrogram of a recent oak fragment featured abundant lignin markers reflecting uncharred biomass. This pyrogram was omitted from the discussion because of the divergent composition of the pyrolysate. Pyrolysis-GC/MS studies on recent or laboratory charcoal have shown that many fragments produce lignin markers upon pyrolysis [37,40]. It is possible that only one charcoal fragment produced these methoxyphenols due to uncharred primary biomass in the other fragments already being degraded during storage in soil. Again, the differences between the species of a given age were small. Suffice it to mention that the contribution of dibenzofuran in general appeared larger for birch than for *Quercus* and Fabaceae-derived charcoal.

We were able to calculate 'average pyrograms' for six periods covered by PRD-4 (Fig. 5) because of the similarity of pyrolysis product retention times between samples and low baselines. It is not common practise to manage chromatograms this way, but it serves well to illustrate the main age-related differences between chromatograms. Each scan's contribution to the TIC was calculated to correct differences in signal intensity between samples.

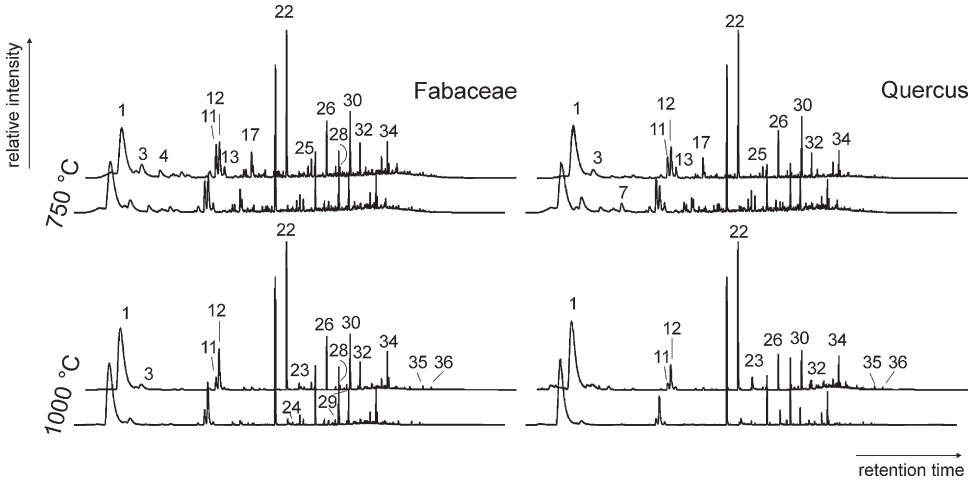

Fig. 4. Total ion chromatograms from *Quercus* and Fabaceae charcoal obtained by pyrolysis at 750 °C (two replicates) and at 1000 °C of the residues (two replicates). Numbers refer to pyrolysis products depicted in Fig. 2.

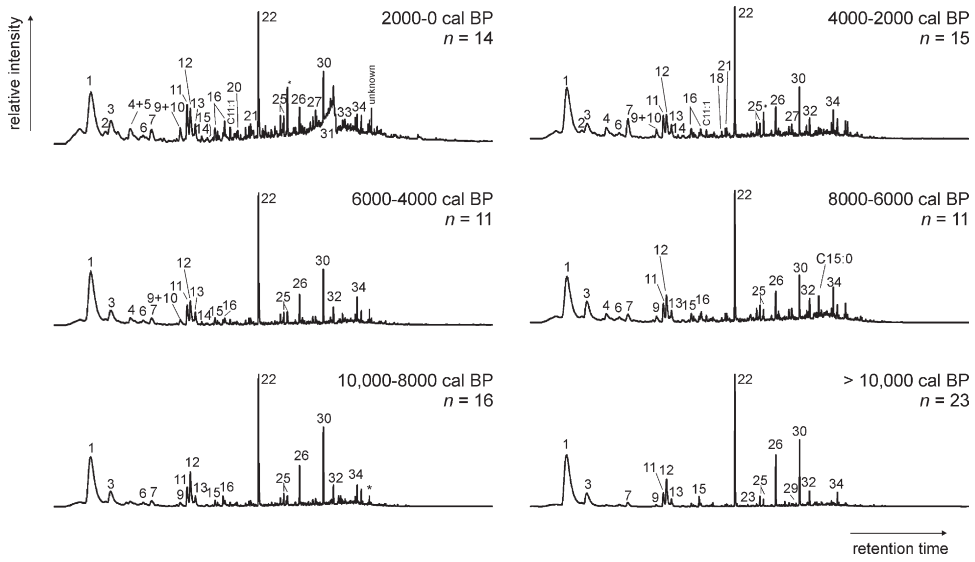

Fig. 5. Average total ion chromatograms of charcoal categorised into 6 age classes (calculated from *n* individual chromatograms). Numbers refer to pyrolysis products depicted in Fig. 2.

Charcoal formed during the last 2000 yrs ($n = 14$) produced a more diverse pyrolysate than older charcoal (Fig. 5). Some of the recent charcoal fragments contained an uncharred core showing high peak intensities for levoglucosan, a pyrolysis-GC/MS product of intact polysaccharide in BC [26]. Thus, polysaccharides can still be recognised as levoglucosan, even after pyrolysis at 750 °C for 10 s. In addition, the youngest chars were characterised by larger contributions of furans, short chain fatty acids (C_6–C_{11}), C_{11}–C_{20} *n*-alkanes/*n*-alkenes, phenols, pyrroles, pyridines, indole and dichlorobenzene, the latter of which is of unknown source. Many of these compounds reflect uncharred or weakly charred and probably biodegraded biomass, with a possible additional fraction of artificially charred polysaccharide (furans). Nonetheless, benzene, toluene and naphthalene were prominent in these pyrograms as well, reflecting the more severely altered (or 'more condensed') BC fraction in these charcoal fragments [71]. The pyrolysates were increasingly less diverse with charcoal age: furans, levosugars, phenols, pyrroles and aliphatics (*n*-alkanes/*n*-alkenes and fatty acids) diminished, while the relative contributions of benzene, PAHs (mainly naphthalene and biphenyl) and benzonitrile increased. The pyrolysis fingerprints of the charcoal fragments older than 10,000 yrs resembled those obtained from the 1000 °C residue series from PRD-2. This is interpreted as an increased contribution with age of those BC products deriving from the relatively thermostable and therefore likely more condensed fraction of BC.

While benzenes and PAHs are obvious pyrolysis products of BC, the N-containing pyrolysis products deserve a more detailed discussion. Many authors reported N enrichment as a result of thermal treatment or fire [42], but the form in which the N occurs is still source of debate. Nitrogen-15 NMR studies showed that amidic N was partially transformed to pyrrole- or indole-like heterocyclic structures during thermal modifications [38,68,69,72]. However, pyridine-type N may have been underrepresented by ^{15}N NMR [73,74]. With regard to pyrolysis-GC/MS, previously reported N-containing products of BC-rich samples include quinoline, indole, pyridines, pyrroles and benzonitrile [4,35,75], but these compounds are also found in the pyrolysates of non-charred organic matter [76]. In this study a novel series of aromatic nitriles were observed in addition to these compounds: 1,x-benzenedicarbonitriles, 1,x,x-benzenetricarbonitrile, naphthalene carbonitriles, 2-phenylpyridine and a biphenylcarbonitrile. Furthermore, a long-chain aliphatic nitrile could have been present in some pyrolysates as oleanitrile ($C_{18}H_{33}N$; characteristic *m*/*z* 122 + 263). Pyrollic N was abundant only in the more recent charcoals ($\leq$ *ca.* 200 yrs). The nitriles accounted for most of the peak area from N-containing pyrolysis products (81 ± 12%). This nitrilic fraction seemed to increase with age ($r^2 = 0.62$, $P < 0.001$) and was enriched in the non-pyrolysable residue (re-pyrolysed at 1000 °C; Fig. 4). Both observations suggest that these aromatic nitriles originated from relatively thermostable/condensed BC. Aromatic nitriles are sometimes related to microbial degradation products of proteins [61]), but it is very unlikely that the benzonitriles of this study are biodegradation products since those samples in which it is concentrated have very low levels of other biodegradation products such as furans and pyrroles. The nitriles may have formed upon e.g. dehydration of aromatic amides or amines [67,76,77]. Alternatively, ring scission and subsequent electron configuration rearrangement of quaternary or pyridinic N in polyaromatics, which may be abundant in severely charred biomass [78,79], may produce aromatic nitriles upon ring cleavage. The potential occurrence of pyridine-like heterocyclic N in BC deserves further research. Finally, additional N may have been present in the charcoal as amidic N but not reflected in pyrolysates because of their poor observability in pyrolysis-GC/MS [30,80]. Some nitriles were also produced upon pyrolysis of asparagines and proline at 870 °C, indicating that secondary rearrangements can culminate in the neoformation of N-containing aromatic nitriles [81]. Nitrogen K-Edge XANES (X-ray absorption near-edge structure) is capable of distinguishing pyrrole, amide and pyridine N and might therefore provide the answer to this matter [82,83].

The changes in charcoal composition with age can be summarised as a reduced diversity of products, a decrease in markers of non/weakly-charred biomass and a relative increase in the products of relatively condensed BC. These results suggest that, unsurprisingly, the more condensed aromatic network of BC is selectively preserved during long-term storage in soil. On the other hand, the TIC increased significantly from ~500 to 12,500 yrs old charcoal ($r^2 = 0.62$, $P < 0.001$), despite the decreasing contribution of pyrolysis products that originated from relatively easily pyrolysed precursors (e.g. furans and alkanes/alkenes). This observation suggests that the condensed aromatic network becomes more susceptible to pyrolysis overtime. Selective degradation of uncharred or weakly charred biomass in combination with partial depolymerisation of the condensed aromatic backbone may well explain the results presented in Fig. 5.

The majority of evidence so far clearly indicated that the evolution of BC during storage in soils is governed by progressive surface oxidation, principally carboxylation [5,6,38,84]. Carboxylated BC derivatives were not observed in this study because polar substances are not easily transported through the non-polar GC column used here and because pyrolysis promotes decarboxylation [28,85]. Indeed, THM (a pyrolysis method which provides protection of functional groups through methylation [86]) of a series of charcoal fragments from soil PRD-1 produced a large suite of carboxylated aromatics, including benzene carboxylic acids (benzene with 1–6 methylated carboxylic groups) [47]. Using THM, de la Rosa et al. [87] found a trimethoxybenzonitrile and benzene- and naphthalenecarboxylic acids in chlorite oxidation-resistant BC-like organic matter, suggesting that the nitriles may derive from oxidised BC moieties. Benzene polycarboxylic acids were also detected by GC/MS after ruthenium tetroxide oxidation treatment of refractory organic material, and most likely derived from BC as shown by high-resolution transmission electron microscopy (HRTEM [88]). Oxidative degradation of BC produces smaller and highly reactive aromatic products [89]. We suggest that the gradual oxidation and associated depolymerisation of BC increased the pyrolysability of previously more condensed structures, thereby producing better chromatograms with increasing age of the charcoal.

4. Conclusions

With regard to the objectives of this study, it is concluded that: (1) Using the BC-optimised pyrolysis-GC/MS method, charcoal produced principally benzene, toluene, naphthalene, biphenyl, dibenzofuran and benzonitrile. Any material producing mainly these compounds upon pyrolysis most likely contains large amounts of BC. (2) With age, these same products increased in proportion to the products of uncharred or weakly charred biomass (furans, pyrroles, *n*-alkanes/*n*-alkenes). Charcoal fragments of the same age but from different plants produced very similar pyrolysates, and thus the method would be unable to distinguish charcoal from different species. (3) Signal intensity improved with age, suggesting that charcoal-BC becomes more pyrolysable. Nonetheless, markers of easily pyrolysable biomass diminished with age. It is concluded that the relatively condensed aromatic backbone of the charcoal depolymerises with age thereby becoming more susceptible to pyrolysis. Finally, the unexpected similarity between the chromatograms in general suggests that under the conditions of this study the pyrolysis of BC is reproducible and follows certain rules.

Acknowledgements

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MANUSCRIPT 7

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Holocene vegetation changes in NW Iberia revealed by anthracological and palynological records from a colluvial soil

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A HOLOCENE RESEARCH PAPER

Abstract: Macroscopic charcoal, pollen and non-pollen palynomorphs were isolated from a colluvial soil located on a small hill in Campo Lameiro (NW Spain) in order to elucidate the vegetation history of the area and its relation to fire and human activities. The presence of macroscopic charcoal throughout the 2.10 m thick soil (42 samples) is evidence of frequent fires during the last *c*. 6300 years. The charcoal record was dominated by *Quercus* (probably *Q. robur*), Ericaceae (probably *Arbutus unedo* and *Erica arborea*) and Fabaceae (mainly *Genista* type). Abrupt changes in the charcoal assemblage are less explicit in the pollen sequence, probably as a result of pollen inflow from the downhill surroundings of the study site. Combined results indicated that the original oak woodland was gradually replaced by pyrophytic shrubs (Ericaceae and Fabaceae) as a result of fire recurrence. Non-pollen palynomorphs strongly suggested that vegetation was deliberately ignited by past human societies to facilitate grazing. No evidence of local agricultural practices was found. Episodes of accelerated shrubland expansion occurred *c*. 6000–5500 cal. BP, *c*. 4000–3500 cal. BP and *c*. 1700 cal. BP, the latter of which caused the definitive settlement of shrublands dominated by Ericaceae and Fabaceae which are nowadays widespread in NW Iberia.

Key words: Charcoal analysis, pollen, non-pollen palynomorphs, fire, vegetation dynamics, NW Iberia.

Introduction

The formation of open-cultural landscapes as the outcome of burning vegetation by prehistoric societies has been studied extensively, especially in Europe (Clark *et al.*, 1989; Tinner *et al.*, 1999; Santos *et al.*, 2000; Carcaillet *et al.*, 2002; Ruddiman, 2003; Gerlach *et al.*, 2006; Hajdas *et al.*, 2007). However, in Galicia (NW Spain), few studies have been undertaken to relate human activities to the fire regime and formation of the present-day landscape, even though it is well-known that fire has played an essential role in the landscape evolution during the Holocene (Bouhier, 1979; Martínez Cortizas, 2000; Fábregas Valcarce *et al.*, 2003). Fire, climate change, human activities and vegetation dynamics form a complex cycle of cause and effect that is difficult to disentangle (Vannière *et al.*, 2008; Cordova *et al.*, 2009).

In this paper, we attempt to discern the evolution of the local and regional Holocene vegetation in NW Iberia under the impact of the human population. For this purpose, wood-charcoal and pollen analyses have been carried out in the colluvial soil of PRD-2, in which charcoal accumulations have occurred as a result of recurrent fires. The PRD-2 profile represents the last *c*. 6300 years of soil accumulation (Costa Casais *et al.*, 2009). Knowledge on landscape evolution and human activities in this region is paramount because the area harbours one of the largest concentrations

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of rock art in the NW Iberian Peninsula which is bound to become a major tourist attraction after the completion of a museum (http://www.campolameiro.com/centro_inter_cast.html).

In the NW Iberian Peninsula, organic matter-rich colluvial soils (Atlantic rankers) are widespread (Carballas *et al.*, 1978). Environmental proxies obtained from such soils can be used for reconstructing past landscapes and their evolution (Kalis *et al.*, 2003). Pollen and charcoal are two such proxies which enable to us to establish the relationship that links fire, human activity and vegetation change. Such a combination of tools also provides information on the spatial scale of environmental change. While macroscopic charcoal generally reflects local wood burning events, pollen analyses might provide a relatively complete image of vegetation dynamics on a more regional scale, including unburned areas (Carrión, 2005; Colombaroli *et al*., 2008; di Pasquale *et al.*, 2008). Unlike the pollen analysis, the charcoal record lacks information on grasses, and often on sedges and ferns, because they have either been completely reduced to ashes or are difficult to identify on the basis of their anatomy (Emery-Barbier and Thiébault, 2005). Differential production, transport and degradation rates of pollen and charcoal for the different species introduce a bias into both data sets and further discrepancies appear among them (Havinga, 1984; Figueiral and Mosbrugger, 2000; Scott *et al.*, 2000). Consequently, palynological and anthracological records must be interpreted and compared with caution.

Apart from determining the composition of vegetation by means of pollen types, palynological studies may provide information on other site conditions using non-pollen palynomorphs (NPPs). Most NPPs are locally produced and may be related to a specific soil trophic status (eg, Zygnemataceae, Cyanobacteria), to the presence of specific soil components (*Chaetomium*/charcoal, *Sordaria* and *Sporormiella*/animal excrements, etc.), or to geomorphological processes (*Spyrogira*/flooding, *Glomus*/soil erosion) (López Sáez *et al.*, 1998; van Geel, 2001). Therefore, NPPs can be used in combination with pollen and charcoal records to obtain a deeper understanding of vegetation dynamics and environmental conditions.

In this sense, this paper aims to (1) understand the vegetation dynamics of Campo Lameiro and the role of fire therein and (2) identify human activities and their link to vegetation and the fire history since the mid Holocene.

Geographical and archaeological setting

Campo Lameiro is located in a subcoastal area, 25 km east from the Atlantic Ocean in the temperate region of the NW Iberian Peninsula (Figure 1a). Here the climate is characterised as mild and humid, with mean annual temperatures of 15°C (9°C in winter and 21°C in summer) and a mean annual precipitation of 1200 mm (concentrated in autumn and winter) (Martínez Cortizas and Pérez Alberti, 1999). Despite the high annual rainfall, the vegetation of this area is susceptible to ignition because of the dry summer period. Current vegetation is a mosaic of shrubs (heather, gorse and broom), trees (pine, eucalyptus and oak), ferns (common bracken) and grasses.

The Paredes section (PRD) in the Rock Art Park of Campo Lameiro (42°32′47.86″N; 8°31′40.42″W) is located on a hill called *Monte Paradela* (190–330 m a.s.l.), which is surrounded by several small streams. Therefore, it is isolated from sediment pathways other than those on the hill itself (Figure 1b,c). In the summer/autumn of 2008, a series of archaeological structures, which probably evidence (temporary) small-scale human settlements, have been excavated from the museum's construction site (Figure 1c). Nevertheless, the archaeological function of the petroglyphs and

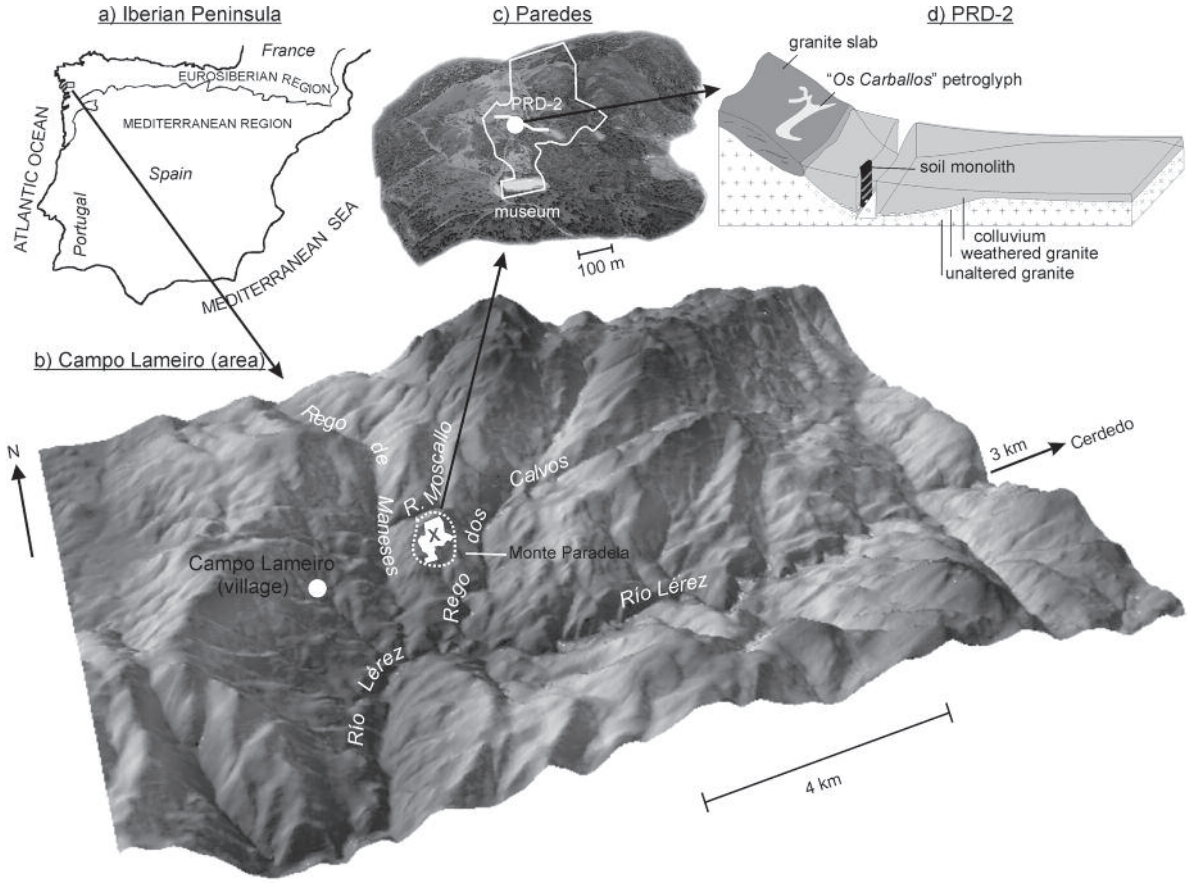

Figure 1 Location of the study area (a–c) and sampling site (d). Greyscale on 3D plot represents altitudes from 100 to 508 m a.s.l.

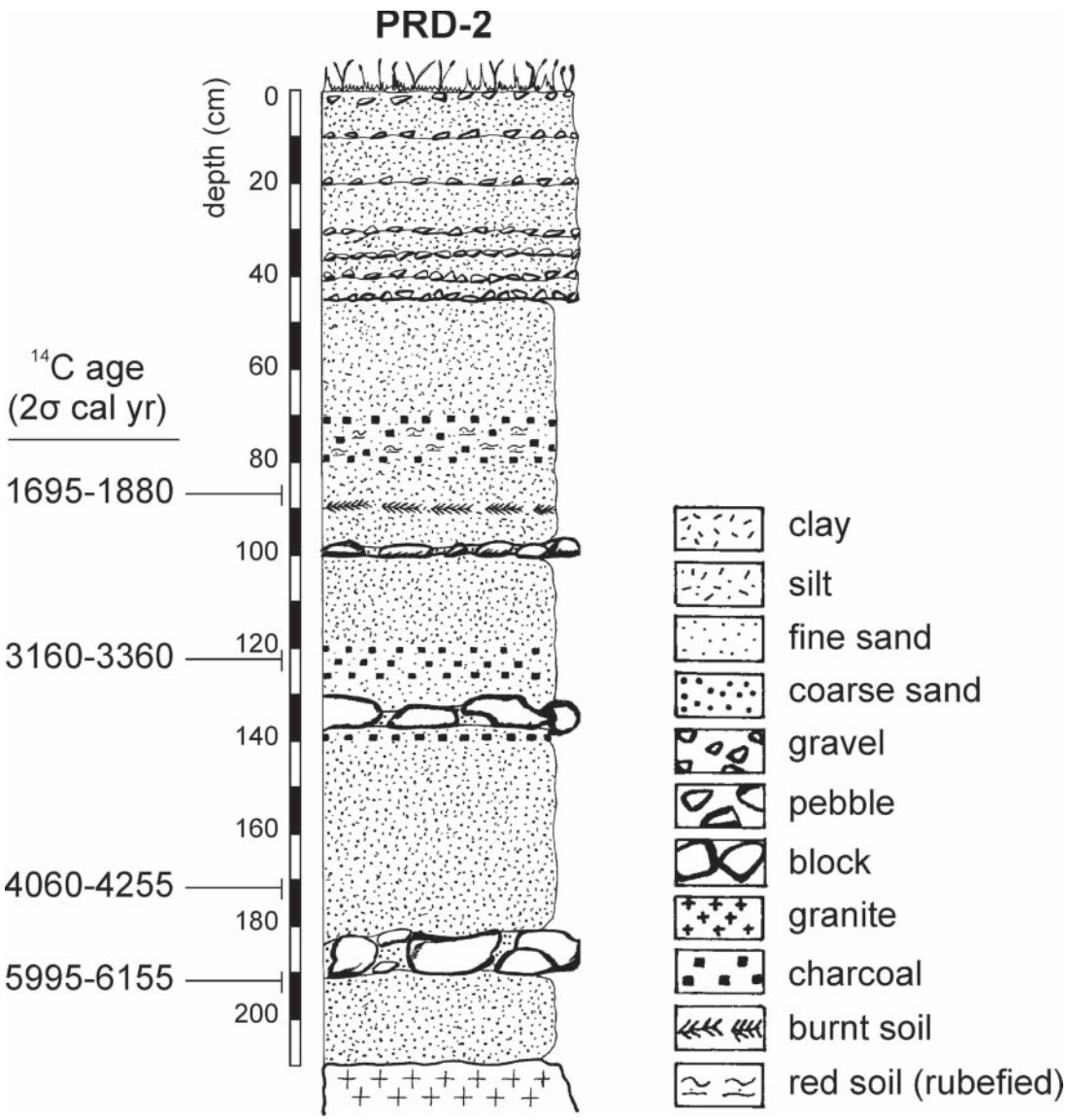

Figure 2 PRD-2 soil profile with radiocarbon ages (drawing courtesy of Manuela Costa Casais)

the potential housing structures are poorly understood. The almost complete lack of archaeological materials (eg, pottery) obtained from the area suggests that only a small number of humans had settled there and that they did not inhabit the site over long continuous periods.

Material and methods

The soil under study (PRD-2) is one of a series of five profiles obtained from the Paredes section in Campo Lameiro (Figure 1d). Located at an altitude of 310 m a.s.l., it is next to a rock art panel called '*Os Carballos*' (Santos Estévez, 2005). In 2003, a trench was dug in the colluvial sediment next to this petroglyph. A 2.10 m thick soil monolith was collected from this trench (Figure 1d) and was cut into 5 cm intervals to obtain 42 soil samples (Figure 2). No evidence of either fireplaces or other domestic activities was found during the excavation of PRD-2. The soil material (including charcoal) had probably accumulated through natural sedimentation, since we have no evidence of eg, fireplaces or other domestic activities. For this reason, it is considered an 'off-site' record. This soil is classified as haplic Umbrisol International Union of Soil Sciences–ISRIC World Soil Information–FAO (IUSS, 2006). In Western Europe, such soils are traditionally referred to as Atlantic rankers and they generally develop in humid areas under temperate conditions with high primary production and strong weathering of granite.

Radiocarbon ages of four soil organic matter samples obtained by the standard acid-alkaline-acid extraction protocol of the Ångstrom Laboratory (Uppsala University, Sweden) are shown in Figure 2. ^{14}C dates were calibrated using CALIB 5.0.1 (Stuiver and Reimer, 1993). It is quite unlikely that the buried layers of PRD-2 received significant amounts of fresh organic matter because the soil is rich in poorly crystalline Al phases, which limits organic matter mobility, and also because humic acids were used for ^{14}C measurements (lacking fresh organic matter). This was confirmed by the molecular characterisation of the organic matter using the pyrolysis-GC/MS method (Kaal *et al.*, 2008a, b). Therefore, the ^{14}C ages obtained are unlikely to be biased by rejuvenation. A comparison made with ^{14}C dated samples from other soils in Campo Lameiro indicates that the surface of PRD-2 is erosive and roughly 200–600 years old.

Macroscopic charcoal (> 2 mm) was separated from the soil samples by wet sieving and was weighed after drying. The botanical identification of charcoal was done using a metallurgical microscope at a magnification of between 100 and 1000

(Vernet, 1973; Vernet *et al.*, 1979). The anatomical patterns observed were compared with a reference collection of carbonised wood, anatomy atlases and specialised bibliography (Metcalfe, 1960; Metcalfe and Chalk, 1950; Greguss, 1955, 1959; Jacquiot, 1955; Jacquiot *et al.*, 1973; Schweingruber, 1978, 1990) so that charcoal fragments could be identified to the species, genus or family level. When a higher magnification was required, charcoal was examined with a scanning electron microscope (SEM). A total of 2063 fragments have been identified. Although the mass of the fragments is sometimes used to express relative species abundance (eg, Carcaillet and Thinon, 1996), in this paper we used the number of fragments as proposed by Delhon (2006).

Other dendrological features (growth-rings curvature, radial cracks and vitrification) were examined under low magnification (Marguerie and Hunot, 2007). The degree of ring curvature was determined for large charcoal particles (> 5 mm radius and > 3–4 mm tangential width) by estimating the parallelism of rays. The growth-rings of these particles were classified as being weakly, intermediately or strongly curved. This classification enables the estimation of the maturity of the plant when it was burnt. A large proportion of charcoal with strongly curved rings reflects the burning of small calibre wood (Marguerie and Hunot, 2007). The presence or absence of vitrified elements and radial cracks in the charcoal was denoted qualitatively. Radial cracks in charcoal can be, among other causes, an indicator of the burning of green wood, which can be accounted for by rapid dehydration and conflagration (Théry-Parisot, 2001). Vitrification results in a gradual fusion of cell walls which creates a glass-like surface and a low pore volume of the charcoal (Pulido-Novicio *et al.*, 2001), thus making botanical identification difficult. The factors which cause this phenomenon are still a matter of debate, but most authors agree that it generally occurs when one of the following fire parameters are met: (1) high temperature (Fabre, 1996; Tardy, 1998), (2) high moisture content of the burnt wood (Thinon, 1992) and (3) burning of green wood in general (Scheel-Ybert, 1998).

Pollen and NPPs were counted using the same volume of preparation (5 g/sample). Pollen grains were extracted using the classical method of concentration in a heavy liquid (Thoulet solution, d=2) after treatment with HCl and HF (Faegri and Iversen, 1989). The pollen results are provided as the percentage of the total pollen sum (approximately 500) accounted for by a given pollen taxon. The Cyperaceae, ferns and NPPs were not added to the total pollen sum, although their frequencies are expressed as percentages of the pollen sum (van Geel *et al.*, 1981). Pollen diagrams were plotted in Tilia and TiliaGraph 2.0 (Grimm, 1992). Here we provide a summary of the results of the pollen analysis. For a more detailed description of the pollen and NPP records, please refer to López Sáez *et al.* (2009).

Results and discussion

Charcoal

Macroscopic charcoal was present in all the samples, which is a sign of frequent burning on a local scale (Clark *et al*., 1998; Blackford, 2000; Gardner and Whitlock, 2001; Lynch *et al*., 2004) for the past *c*. 6300 years. The taxonomical diversity of the charcoal was poor: only 13 taxa were identified (Figure 3), four of which (*Erica* sp., Fabaceae, deciduous *Quercus* and *Arbutus unedo*) accounted for 98±5% of the charcoal (mean and standard deviation for 41 samples). Although some samples, particularly those from the top of the soil, provided only a small number (20–30) of identified charcoal fragments (see Appendix 1), most spectra are statistically meaningful as they have been tested in 'saturation curves' (Chabal, 1997) (Figure 4). In addition, we found no significant relationship between the amount of charcoal fragments analysed and the number of taxa identified.

Heathers were the most frequently observed taxonomical group (53±37%). According to the ray width criteria proposed by Queiroz and Van der Burgh (1989), the heathers in PRD-2 mostly derived from *Erica arborea* (rays 5–7/8 cells wide) (figure 3, photos 4–5), which was confirmed by the pollen analysis (see below). Some *Calluna vulgaris* (uniseriate rays, small vessels in a transverse section) could have been present, although scalariform perforations of 2–3 bars high were not observed. Currently, the NW Iberian Peninsula harbours a large diversity of heather species which often occur as the shrub stratum in light oak forests. Heather communities may develop on sunny slopes in combination with *Genista tridentata* to create a formation that adapts well to soil degradation and fire recurrence (Rodríguez Guitián *et al.*, 1996). In NW Iberia, charcoal derived from heather has been frequently observed in archaeological layers and fireplaces (Figueiral, 1993; Carrión, 2005), which is probably related to the flammability and excellent qualities for fire kindling of heather wood.

Two groups of genera from the Fabaceae family (23±21%), F. type *Genista* and F. type *Ulex* (Figure 3, photos 6–7) were identified from the anatomical key characters proposed by Marguerie and Hunot (1992). Fabaceae of the *Genista* type have relatively few multiseriate rays and the cells are narrow in the transversal and tangential sections. On the radial section, ray cells of the *Ulex* type are relatively large and exclusively composed of square and upright cells. According to these criteria, Fabaceae type *Genista* was predominant. Currently, the most frequent Fabaceae genera in the NW Iberian Peninsula are *Genista* (*G. florida*, *G. cinerea*), *Ulex (U. parviflorus)* and *Cytisus* (*C. striatus*, *C. scoparius*, *C. multiflorus*) (Costa *et al*., 1997). The majority of these legumes are heliophytic and pyrophytic species that form part of substitution communities on degraded soils.

Oak species account for 17±20% of the charcoal from PRD-2. Deciduous *Quercus* can be distinguished from evergreen species when the growth-ring boundary is observed because deciduous oaks present conspicuously larger vessels in earlywood (Greguss, 1959), corresponding to the growth of new foliage in spring (Figure 3, photo 11–12). The criteria for oak species determination based on the presence of rows of large vessels in earlywood (Heinz, 1990) are not suitable for small-sized charcoal fragments. In the NW Iberian Peninsula, pedunculate oak (*Quercus robur*) is currently the most abundant.

Arbutus unedo (5±10%; Figure 3, photo 1) has its ecological optimum in the Mediterranean region and is less widespread in Atlantic areas. Formations with strawberry trees are common in open oak communities. After a fire, this species sprouts easily with several new shoots, rendering it an effective competitor (Romo Díez, 1997; Costa *et al*., 1997).

Other taxa identified were *Betula*, *Clematis*, Pomoideae and *Prunus*. One taxon was identified as common bracken (cf. *Pteridium aquilinum*) (Figure 3, photo 10) according to some characteristic anatomical patterns such as vessels packed in tangential to oblique groups on the transverse section (Schweingruber *et al.*, 2006: 72). The spores of this species were found on the pollen slides from PRD-2, and Figueiral (1996) also identified its charcoal in NW Portugal. However, vitrification of the majority of fragments inhibited unequivocal identification. There was also a high percentage (12.5%) of indeterminable charcoal, sometimes because of the small size of the fragments, but more often because of anatomical alterations that complicate the botanical identification.

Figure 5 shows the depth profile of the four dominant charcoal taxa (*Erica*, Fabaceae, *Quercus* and *Arbutus*), macroscopic charcoal content (> 2 mm) and the proportion of wood with strongly curved rings. The PRD-2 sequence begins *c*. 6100–6300 cal. BP

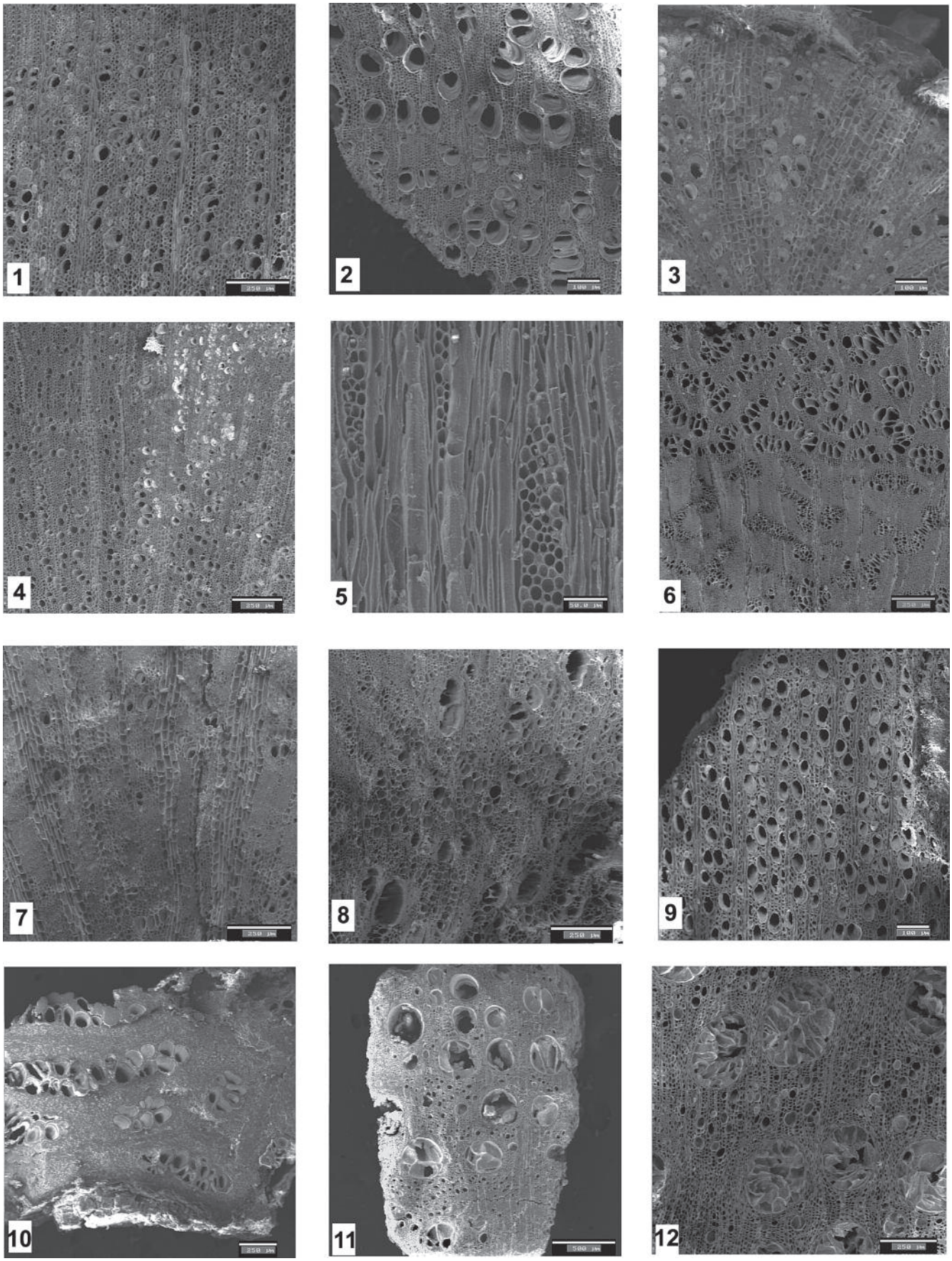

Figure 3 SEM images of some taxa identified in PRD-2. (1) *Arbutus unedo*, transversal section; (2) *Betula* sp., transversal section; (3) *Clematis* sp., transversal section; (4) *Erica* sp., transversal section; (5) *Erica* sp., tangential section; (6) Fabaceae tp. *Genista*, transversal section; (7) Fabaceae tp. *Ulex*, transversal section; (8) Fabaceae, transversal section with radial cracks; (9) Pomoidea, transversal section; (10) cf. *Pteridium aquilinum*, vitrified transversal section; (11) deciduous *Quercus*, transversal section; (12) deciduous *Quercus*, transversal section, detail of tyloses

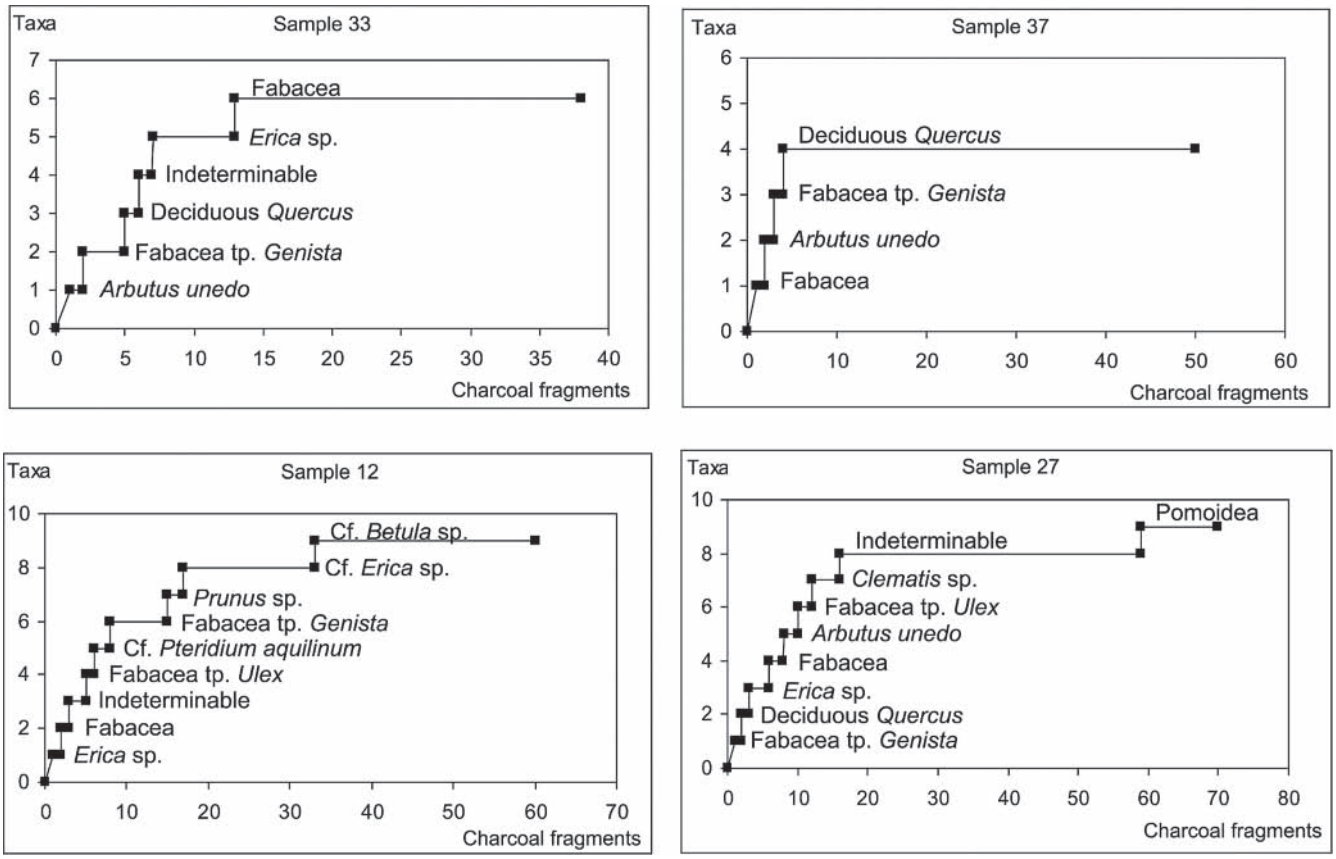

Figure 4 Saturation curves of four samples from PRD-2, as examples of poor charcoal-content levels (37, 33) and samples with 'high' taxonomical diversity (12, 27). In the former samples, no appearance of new taxa is expected; in samples 12 and 27, only some indeterminable and 'cf' taxa (with the exception of Pomoidea in sample 27) impede the complete stabilization of the curves. This method determines the number of charcoal fragments to be identified in order to obtain the optimal representation of the flora (Chabal, 1997). In most samples of PRD-2 profile, the curves showing the appearance of new taxa are completely stabilized

when most charcoal derived from Fabaceae and *Quercus*. Between 5995–6155 and *c*. 4070 cal. BP, the contribution of *Quercus* decreased from ~65% to ~35%, with a corresponding increase in *Arbutus unedo*. Stones were found in this soil layer (Figure 2). A hiatus in soil stratigraphy of between 185 and 190 cm in depth (Costa Casais *et al.*, 2009) might conceal an even steadier decline in *Quercus* contribution. Thereafter, a second decline in *Quercus* (from ~35% to ~10%) occurred shortly after 4000 cal. BP (160–165 cm) when *Erica* increased from 20% to 47% of the charcoal. The increased proportion of *Erica*-derived charcoal corresponded to an increase in the proportion of wood with strongly curved rings (Figure 5) and charcoal with radial cracks (Figure 3, photo 8), suggesting that relatively mature stands consisting of mainly *Arbutus* and *Quercus* were partially replaced by rapidly rejuvenating heather formations. Ericoid shrubs remained dominant until *c*. 3500 cal. BP, ie, 135–140 cm. The taxonomical composition of the charcoal revealed a strong variation between 140 and 110 cm in depth (*c*. 3500–2800 cal. BP), suggesting rapid vegetation changes that cannot be explained at the current sample resolution. Between *c*. 2800 and 1700 cal. BP (110–85 cm), charcoal from Fabaceae was dominant while *Quercus* gradually disappeared as a result of the formation of heliophyte shrubland. Afterwards at *c*. 1700 cal. BP, a major shift in the charcoal source from Fabaceae to Ericaceae occurred, which coincided not only with a strong increase in macroscopic charcoal content (up to almost 10 g/kg soil), but also with an increase in the percentage of wood with strongly curved rings (Figure 5). The peak in charcoal content also coincided with the highest percentage of charcoal exhibiting radial cracks and vitrification. These results can be interpreted as an accelerated rejuvenation of vegetation as a result of fire regime intensification, which created nearly monospecific heather stands (its proportion in some samples exceeded 95%). After the charcoal peak, however, the soil macroscopic charcoal content declined progressively and the proportion of charcoal with strongly curved rings (and radial cracks) also decreased, suggesting stabilisation of the heather formation that was probably subjected to a less intense fire regime. The settlement of this relatively stable and mature scrub vegetation might have been promoted by soil erosion and a gradual soil impoverishment (eg, acidification and fire-induced nutrient loss), so the forest could not develop properly (Giovannini *et al.*, 1990; Martínez Cortizas *et al.*, 2000; Kaal *et al*., 2008c). Indeed, the latest expansion of *Erica* coincided with a peak in coarse (> 2 mm) inorganic soil material which indicates strong erosion.

Some information on fire dynamics can be inferred from these results. The expansion episodes of *Erica* coincide with a clear decline in deciduous *Quercus* charcoal, suggesting that oak is sensitive to fire recurrence (Pausas, 1999). Trabaud (1996) showed that fires in oak woodland reduced total vegetation biomass and taxonomical diversity, and stimulated the expansion of pyrophytic species. In that study, oak regenerated to some extent in the 5–6 years after the fire, unless the site had been burned repeatedly to produce a heather-dominated shrubland. Analogously, the stepwise decline in oak charcoal in the present study was probably associated with rapidly reiterating fire events (supported by the omnipresence of charcoal in the sequence), which partially explains the taxonomic poverty in the charcoal record (Lloret *et al*., 2005; Pausas, 2006). It is difficult to elucidate the total number of fire episodes recorded in the soil or the interval between them because erosive

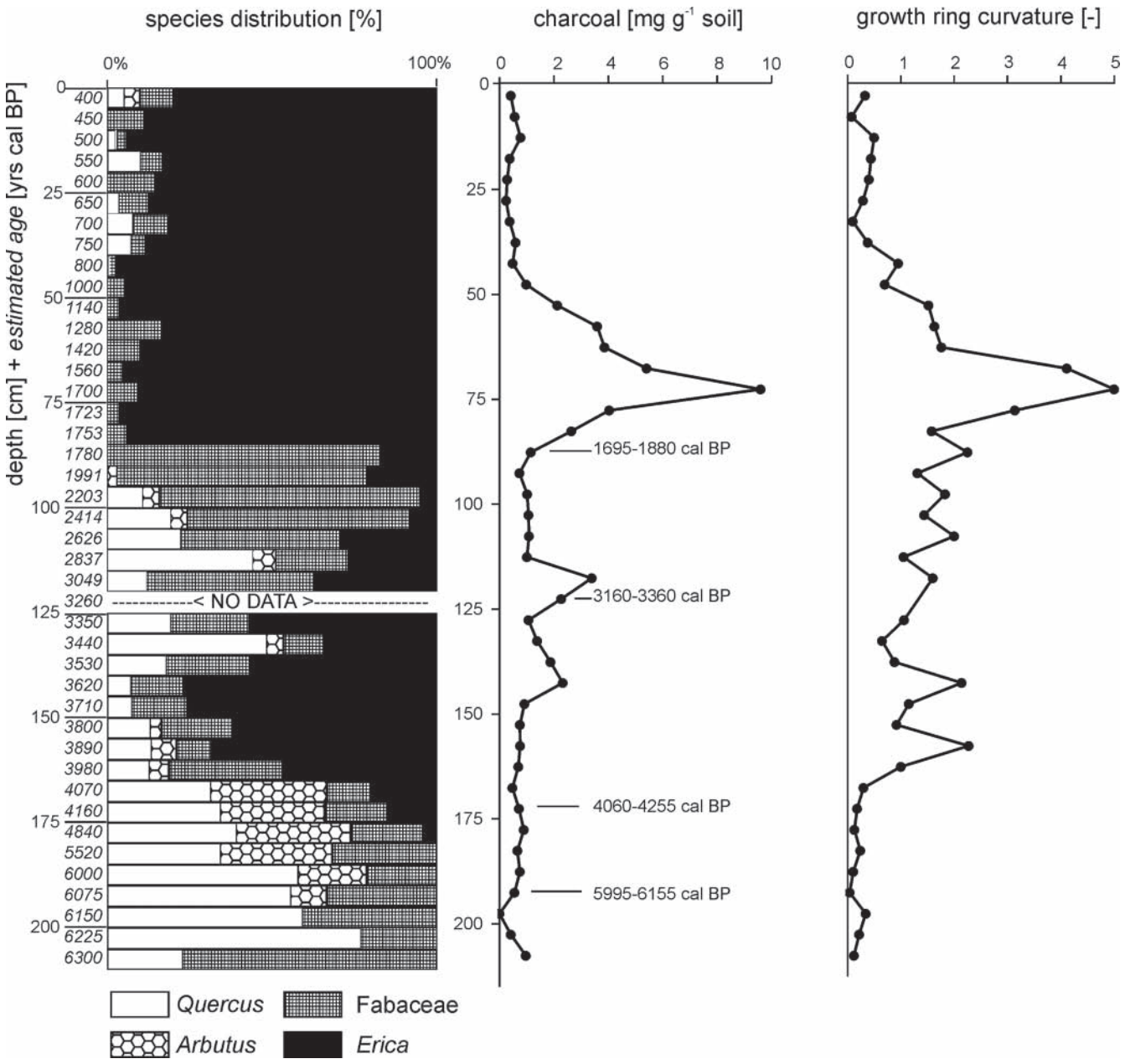

Figure 5 Composition of charcoal assemblages from PRD-2 (simplified), charcoal content and growth-ring curvature (proportion of wood with strongly curved rings) (estimated ages are interpolated from C^{14} dates)

events created the hiatuses in soil stratigraphy and the sampling resolution is insufficient for such purposes. In any case, fires seem to have occurred at short enough intervals to reduce oak regeneration since at least *c*. 2500 cal. BP onwards, which culminated in the definitive settlement of Ericaceae-Fabaceae shrub communities.

Pollen and non-pollen palynomorphs

The pollen record (Figure 6) was dominated by herbaceous plants (20–80%, mainly Poaceae). The dominant tree species was deciduous *Quercus*, while *Alnus* and *Betula* were also observed throughout the profile. A significant proportion of the pollen originated from shrub formations, mainly from *Erica arborea,* but also from *Calluna vulgaris*, *Ulex* type and *Cistus* type. Sedges (Cyperaceae) and ferns (*Pteridium aquilinum*) were also abundant.

The bottom of the sequence, *c*. 6100–6300 cal. BP, showed a high proportion of herbaceous pollen (Figure 6). The woody species were mainly deciduous *Quercus*, *Alnus* sp., *Betula* sp., *Erica arborea*, *Calluna vulgaris* and *Ulex* type. Such pollen assemblages are typical of a light oak-dominated forest, with shrub species and common bracken at open sites combined with dense herbaceous undergrowth. These grasses were mainly Poaceae (35–40%), but species that may be associated with animal husbandry were also present, such as *Plantago lanceolata* and *Urtica dioica* types (Behre, 1981; López Sáez *et al.*, 2003). Between 5995–6155 cal. BP and 4060–4255 BP, the contribution of tree-derived pollen declined abruptly (perhaps associated with the sedimentation hiatus and the stone layer), whereas that of herbaceous pollen increased, suggesting further forest degradation. The simultaneous appearance of coprophilous (dung-living) ascospores of the genus *Sordaria* suggests the presence of local animal husbandry (López Sáez and López Merino, 2007). The NPPs *Glomus* cf. *fasciculatum* and *Pseudoschizaea circula* found in these samples are indicative of soil erosion during this period (López Sáez *et al.*, 1998; van Geel, 2001). The samples at a depth of between 100 and 165 cm (*c*. 4000–2500 cal. BP) are characterised by a decrease in herbaceous pollen and an increase in tree pollen

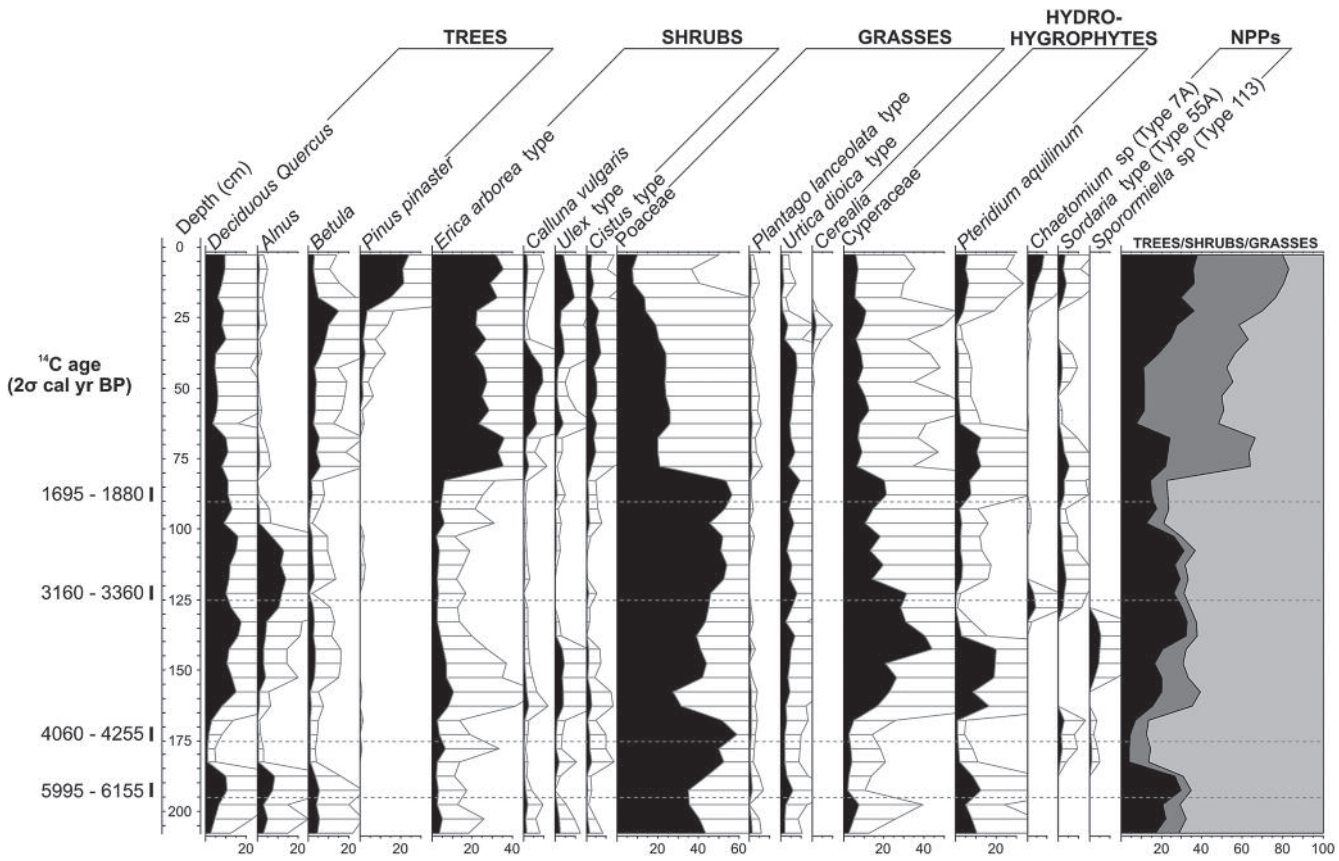

Figure 6 Pollen diagram from PRD-2, including non-pollen palynomorphs (NPPs) percentages (exaggeration is 5%)

(especially oak), Cyperaceae and shrub species (*Erica arborea* type 6–10% and *Ulex* type 5%). The presence of both the coprophilous NPP *Sporormiella* and anthropogenic elements, such as *Plantago lanceolata* and *Urtica dioica* types, are also indicative of human activities in this part of the sequence (López Sáez and López Merino, 2007). In addition, the NPP *Chaetomium* sp. was found, which is thought to thrive on substrates consisting of fire residues (López Sáez *et al.*, 1998, 2000). The high percentage of hygrophilous sedges (Cyperaceae; 20–45%) might indicate more humid conditions in this period. In the second part of this interval, a relative increase in *Alnus* pollen was observed. In the superficial layers of the soil, from a depth of 85 cm towards the surface (*c*. 1700 cal. BP to the present), *Erica arborea* type was the dominant pollen source. The increase of Ericaceae dominated shrub communities (*Erica arborea* and *Calluna vulgaris*) coincided with a decrease in tree and herbaceous pollen and with an increase in the proportion of pollen from ferns (mainly *Pteridium aquilinum*) and *Cistus* type, which is also an evidence of recurrent burning. This period is characterised by forest degradation into shrubland communities ('*matorral*'). *Sordaria* decreased, possibly indicating a reduced pressure from animal grazing, although *Plantago lanceolata* and *Urtica dioica* types were observed. Moreover, pollen from *Castanea* (not shown) and Cerealia were found in surface layers. The percentage of cereal pollen was low (< 3%) and should be considered evidence of agriculture in the proximity of the study site, but not necessarily at the site itself (López Sáez and López Merino, 2005). Pollen from *Pinus pinaster* was abundant in the top 20 cm of the profile.

Charcoal and pollen as proxies of past vegetation

The combined charcoal and pollen records reveal some interesting coincidences. First, both records indicate a first decrease in *Quercus* contribution between *c*. 6000 and *c*. 4000 cal. BP, although the pollen record lacks a corresponding increase in *Arbutus unedo*. Second, the percentages of *Erica* sp. in the pollen and charcoal records were linearly correlated (r^2=0.60; P<0.001; n=41), with both approaches showing a major expansion of ericoid shrubland shortly after *c*. 4000 and *c*. 1700 cal. BP, the latter of which produced a stable and mature formation. Thirdly, some peaks in charcoal concentration (Figure 5) are inversely related to the abundance of tree taxa in charcoal and pollen, which is consistent with other fire–vegetation interaction studies (eg, Colombaroli *et al*., 2008) and modern ecological studies showing a simultaneous trend of woodland cover decline, expansion of shrublands and simplification of the forest structure (Lloret *et al*., 2005; Pausas, 2006). This may be easily explained by the fact that fire promotes the expansion of shrub resprouters (in this case, *Erica*).

But there were also major differences seen between the charcoal and pollen records, such as the relatively small taxonomical diversity of the charcoal. Obviously, non-woody grasses and sedges did not produce macroscopic wood-charcoal, but also many woody species such as *Alnus*, *Betula* and *Pinus pinaster* were not found in the charcoal assemblage, for which an explanation is required. The pollen record provided relatively smooth depth profiles for *Quercus*: the charcoal record suggests that oak diminished in clearly defined phases (*c*. 5500, *c*. 4000 and *c*. 1700 cal. BP), and that Ericaceae-Fabaceae shrubland dominated the site from *c*. 2800 cal. BP onwards. In contrast, the pollen record suggests that tree cover remained significant during the last 2500 years and that the period of oak charcoal decline of *c*. 4000 cal. BP was not observed in the pollen record at all. This discrepancy may be related to the different mobility patterns of pollen and macroscopic charcoal. Most authors agree that unlike microscopic charcoal, large particles (> 125–500 μm in diameter) are not transported over long distances because they settle within or close to

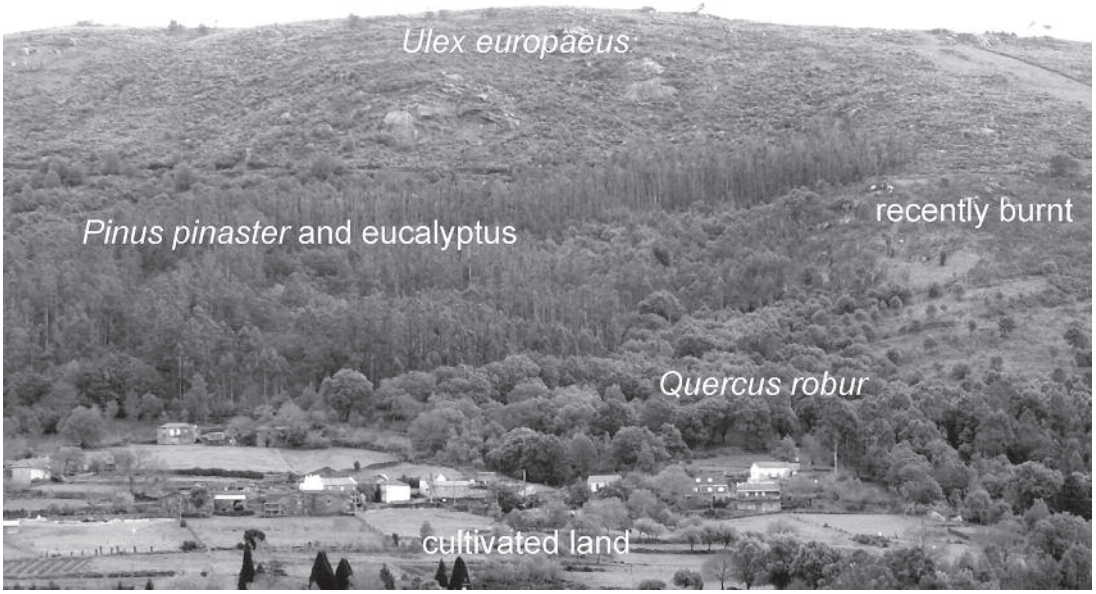

Figure 7 Typical vegetation sequence on a slope near Cerdedo (Pontevedra, Galicia, NW Spain): agriculture and animal husbandry in the valley; oak and eucalypt/pine on the midslope and *Ulex europaeus* on the upper part of the hill

the burned area, which is in agreement with the often-observed rapid decrease in charcoal influx with increasing distance from the fire edge (Clark *et al.*, 1998; Blackford, 2000; Gardner and Whitlock, 2001; Lynch *et al*., 2004; Colombaroli *et al*., 2008). This, however, does not imply that the macroscopic charcoal in Campo Lameiro is immobile because the erosive events in areas subjected to colluviation can also transport heavier and denser materials such as gravel and stones. Nonetheless, we consider that the macroscopic charcoal from PRD-2 must have been produced in the vicinity of the site, at a few hundred metres away on the summit of the hill at the most because these particles cannot be transported uphill (the convectional uplift of macroscopic charcoal during fire is less relevant and less susceptible to wind transport). In addition, the profusion of large charcoal fragments (> 5 mm) may be considered indicative of the very local nature of the charcoal record. On the contrary, however, pollen is transported over long distances so that the pollen record represents the vegetation on a more regional scale. Consequently, the pollen-producing vegetation, that is located further from the study site, is represented by the pollen record but not by the charcoal one. This is especially important for the present case study in a small area on top of hill that undergoes forest regression uphill because of fires: charcoal must be very local while the pollen rain from the lower areas can be easily transported from the nearby valleys and footslopes covered with relatively intact forest vegetation. Uphill pollen transport partially explains the higher taxonomical richness for pollen than for charcoal.

Traditionally, the highland areas of Galicia ('el monte') were subjected to slash-and-burn practices and used as pasture, whereas land use in the relatively fertile soils in the valleys did not involve fire (Criado Boado, 1993). Furthermore, the higher moisture content of the soils on the lowlands may have favoured forest communities and reduced fire sensitivity. It may therefore be assumed that human-induced burning and the consequent degradation of oak forest started in the highlands (the study area) and that the oak pollen found in the soil studied originated largely from areas situated downslope. Pollen input from the surroundings of the site may thus explain why the long-term decline in *Quercus* charcoal was not as evident in the pollen record. Similarly, *Alnus glutinosa* in the NW Iberian Peninsula today is concentrated in the humid river valleys (Rodríguez-Rajo *et al*., 2004). A typical vegetation sequence (Bouhier, 1979; Criado Boado, 1993; Ballesteros, 2003) is still evident at Cerdedo, located ~12 km east of Campo Lameiro (Figure 7): cultivated land and riverside vegetation (eg, *Alnus*) in the valley, oak formations on the lower part of the hill and shrub communities on the upper part (simplified description), in this case with *Pinus* and *Eucalypt*s plantations in between. In short, *Quercus* and *Alnus* pollen from the valleys could have been transported into upland areas such as the site where PRD-2 is located, producing discrepancies between pollen and charcoal records, the latter being a proxy of more local vegetation.

On the other hand, some species were abundant in the charcoal record but sparse in the pollen sequence (such as Fabaceae and *Arbutus unedo*). This discrepancy may have been the outcome of selective degradation or removal of pollen types (Havinga, 1984). With regard to *Arbutus unedo*, the entomophilous pollination of this species might explain the scarcity of its pollen in sediments. However, the fact that charcoal was primarily formed during periods when pyrophytic species were abundant (such as Fabaceae and Ericaceae) probably added to their over-representation in terms of vegetation composition. Within the average time span represented by the studied samples (*c.* 150 yr), short periods of forest recovery produced pollen, but they are not reflected in the charcoal record. A higher sampling resolution would be required to decide this issue.

Holocene landscape evolution

c. *6300–5500 cal. BP*

Soil started accumulating at *c*. 6300 cal. BP, which marked the onset of widespread colluviation in NW Iberia (Fábregas Valcarce *et al*., 2003; Martínez Cortizas *et al.*, 2008, and references therein). During this period, enhanced erosion was often attributed to increased cattle pressure and the corresponding Neolithic system of slash-and-burn agriculture (Martínez Cortizas *et al*., 2008) which led to the decline of the well developed oak formations that dominated coastal forests during the Hypsithermal period (*c*. 8500–6000 cal. BP) (Gómez-Orellana *et al.*, 1998;

Santos *et al.*, 2000; Muñoz Sobrino, 2001; Gómez-Orellana, 2002; Carrión, 2005). An additional purpose of woodland clearance, agriculture, is evidenced by the first appearance of cereal-type pollen and synanthropic species, for example dating back to 6500–6050 cal. BP in the peat record of Tremoal da Pena Veira (Ramil-Rego and Aira Rodríguez, 1993) and to 6450–6240 cal. BP in Chan do Lamoso (Ramil-Rego *et al*., 1994). In the present work, the charcoal from this period was dominated by *Quercus* and Fabaceae, while pollen reflected the presence of the *Quercus-Alnus-Betula* assemblage with significant herbaceous undergrowth, confirming earlier palynological (Ramil-Rego, 1992; Allen *et al.*, 1996; Santos *et al*., 2000; Muñoz Sobrino *et al*., 2005), anthracological (Carrión, 2005) and other macro-remains (García-Amorena *et al*., 2008) studies from NW Iberia. A partially deforested landscape and the presence of pyrophytic shrubs are highlighted by the combined charcoal and pollen results.

c. *5500–4000 cal. BP*

The soil sequence contains a hiatus in the sedimentation record from possibly between *c*. 6000 and *c*. 5500 cal. BP (Costa Casais *et al*., 2009). Therefore, the age estimations in this period are particularly tentative. Around 5500 cal. BP, the percentage of tree pollen decreased in relation to herbaceous one. The presence of *Plantago lanceolata* and *Urtica dioica* types in the pollen record and the peak of NPP *Sordaria* both suggest the use of fire to generate pasture for animal grazing (Martínez Cortizas *et al*., 2008). On the other hand, this phase corresponds to relatively cold and humid conditions associated with the Neoglaciation period (Magny *et al.*, 2006) which, in combination with frequent anthropogenic burning, may well explain this period of significant Holocene environmental change in NW Iberia (Fábregas *et al.*, 2003). The onset of progressive soil acidification in NW Iberia during this period (Martínez Cortizas *et al*., 2008) may have resulted from a combination of nutrient depletion, forest retreat and a worsening of the climate.

c. *4000–3500 cal. BP*

Shortly after *c*. 4255–4060 cal. BP, the contribution of *Erica* increased according to the charcoal and pollen records. However, while the charcoal record suggests a decline in *Quercus* (probably as a result of local scale deforestation on the top of the studied hill), the contribution of *Quercus* pollen increased, indicating the recovery of this species probably in the downhill area. The local rejuvenation of vegetation is supported by the increase in charcoal fragments with a strong growth ring curvature, suggesting rapidly reiterating fires which favoured the expansion of heather shrubland. It is worth noting that the sedimentation rate in PRD-2 seemed to increase significantly in this period (30 cm in ~ 500 yr as opposed to 40 cm in the previous ~ 2300 yr), which may be explained by an intensification of the local fire regime (Martínez Cortizas *et al*., 2009). According to Muñoz Sobrino *et al*. (2001), this is the main period of oak forest regression resulting from human impact and is associated with the consolidation of the agropastoral system in NW Iberia (Carrión, 2005, and references therein). The presence of *Urtica dioica* and a peak in NPP *Sporormiella* (López Sáez *et al*., 2009) suggest that stockbreeding was the objective of clearance. However, this interpretation depends strongly on the assumption that the increase in oak pollen reflects forest recovery in the surrounding areas of the study site rather than at the site itself.

c. *3500–2700 cal. BP*

The pollen record reflects a further expansion of forest by the increase in *Alnus* at the expense of heather and gorse shrubland, and also by the climate amelioration coinciding with the end of the Neoglaciation period (Johnsen *et al*., 1992; Ramil-Rego, 1993; Martínez Cortizas *et al*., 1999; Mighall *et al*., 2006). Two peaks in *Quercus* charcoal might suggest forest expansion during intervals before and after *c*. 3160–3360 cal. BP. This would imply a reduction in ecological pressure exerted by fire, which is in agreement with the decrease noted in *Erica* charcoal. The abundance of *Urtica dioica* and the NPP *Sordaria* suggests that the human activity was intense in the area also during this period.

c. *2700–1700 cal. BP*

The charcoal assemblages obtained from the samples, which were estimated to date to *c*. 3200 and *c*. 1700 years old (^{14}C measurements), were dominated by Fabaceae. The pollen sequence displayed a slight increase of *Ulex* sp., although it was lower than the increase in Fabaceae charcoal. *Alnus* decreased from >10% to less than 1%, while oak pollen also presented a slight reduction. The proportion of herbaceous pollen increased significantly. Combined evidence suggests that the regional forest recovery in the previous phases had come to an end and that a renewed intensification of the burning regime gave way to the expansion of shrubland dominated by legumes.

c. *1700–400 cal. BP*

The latest and most striking event was the rapid colonisation of the area by *Erica* sp. shortly after 1695–1870 cal. BP, which was detected somewhat later in pollen than in charcoal (75–80 cm for pollen, 80–85 cm for charcoal). This delay had also been detected in other studies that compare charcoal and pollen sequences (Carrión, 2005; Colombaroli *et al*., 2008). The coincidence of high percentages of *Erica arborea* and *Cistus* type pollens (Figure 6), both of which are well-known post-fire colonisers (Pérula *et al.*, 2003), reaffirms that the progression of degraded heathland at the expense of deciduous *Quercus* was favoured by fire. In PRD-2, the pollen record shows that the expansion of *Erica* sp. coincided with a relative decrease in herbaceous pollen, thus suggesting that the heather formation was dense enough to inhibit the development of a significant herbaceous understorey. A stable, well developed ericoid community was confirmed by the progressive decrease in wood with strongly curved rings after the initial expansion of *Erica*. Ericaceae-Fabaceae formations are sometimes considered to be the best to adapt to the gradual soil impoverishment induced by fire, and a 'pseudo-climax' series in NW Iberia (Rodríguez Guitián *et al.*, 1996), as documented in other charcoal analyses carried out in Galicia (NW Spain) (Carrión, 2005) and Portugal (Figueiral, 1996).

The first appearance of cereal-type pollen in PRD-2, after *c*. 1700 cal. BP occurred quite late in comparison with the first cereal pollen found in Castro de Penalba (2600 cal. BC) (Aira Rodríguez *et al.*, 1990), located a few kilometres from the study site. This period also showed an increased abundance of *Plantago* type and NPPs, indicating an intensified practice of agriculture and/or animal husbandry. In a peat record from Galicia, Martínez Cortizas *et al.* (2005) found two intense phases of forest decline corresponding to the Roman (*c*. 2000–1600 BP) and Germanic periods (*c.* 1500–1400 BP), which may match the age of the charcoal peak *c*. 1700 cal. BP. In that study, only the Germanic phase related to heather expansion, which might suggest that the charcoal peak

in PRD-2 corresponds to the beginning of the Germanic period in NW Iberia.

In the youngest part of the sequence, pollen from *Pinus pinaster* was found, which is completely absent in the charcoal record. The pollen from this species may have been transported into the study site from longer distances since it is known for its exceptional aeolian mobility (Tormo *et al.*, 1996). *Pinus pinaster* is currently concentrated on the NE part of the hill, more than 100 m away from the studied profile. Although this species is only present in recent chronologies, it has also been identified in pollen sequences from *c*. 8500 cal. BP onwards, such as Mougás, Caamaño, Aguçadoura or Cortegaça for the coastal areas (Gómez-Orellana, 2002), and Laguna de las Sanguijuelas for the eastern Galician mountains (Muñoz Sobrino, 2001). Thus, the appearance of *Pinus pinaster* in recent times may result from spreading after Roman forestation practices, but also from the expansion of the autochthonous pines of the Iberian Peninsula (Figueiral, 1995).

Conclusions

Palaeobotanical studies carried out in Campo Lameiro show that charcoal, pollen and NPPs form a suitable set of proxies to study the relationship that links fire history, vegetation history and human activities.

The pollen record shows that, in the long term, shrub communities expanded to the detriment of grasses and trees. The abundance of charcoal suggests that this development was associated with fire. A comparison of pollen and charcoal records suggests that this process was much more pronounced on a local scale than on a regional one. The recurrence of NPPs is associated with animal husbandry (*Plantago* type, *Urtica* type) which evidences that human disturbance was the main cause of these transformations.

The combined results obtained indicate that the study site is a locally deforested landscape which has been heavily affected by human activities that probably used fire to generate pasture for cattle grazing, which is in line with Bouhier's assertion that the eroded landscape observed today in much of upland Galicia is largely due to the impact of slash-and-burn or similar practices (Bouhier, 1979; Soto *et al.*, 1995).

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Appendix 1

Frequencies of the taxa identified in charcoal from the PRD-2 profile

(Continued)

Sample/ Taxa	*Arbutus unedo*	*Betula* sp.	*Clematis* sp.	*Erica* sp.	cf. *Erica* sp.	Ericaceae	Fabaceae tp. *Genista*	Fabaceae tp. *Ulex*	Fabaceae	Pomoideae	*Prunus* sp.	cf. *Pteridium aquilinum*	deciduous *Quercus*	*Quercus* sp.	Indeterminable	Species minimal N.	Total
1	1			12	2	2	2		2				1		2	3	22
2				16			1	1							1	3	19
3				26	3	2	1						1		2	3	35
4				19	2	4	2					1	3		9	3	40
5				20	2	1	3		1						9	2	36
6				26	2		1		2				1		5	3	37
7				19	2	1	3						2		5	3	32
8				36	3		1		1				3		6	3	50
9				42	3	1			1						13	2	60
10			1	48	2	2	1	1	1						4	4	60
11			1	50	1	3			2						13	3	70
12		1		30	3	2	1	3	3		3	3			11	5	60
13				41	4	1	1		4			1			8	2	60
14				41				1	1						7	2	50
15				48	1	1	2		3						5	2	60
16			1	54			2								3	3	60
17				46		1			3						10	2	60
18				7			7	4	22	1		3			6	4	50
19	1			7			8	1	16			4			9	4	46
20	1			1			4	4	7			8	2		3	5	30
21	2			3			7	5	13				7		7	5	44

Appendix 1 *(Continued)*

Sample/ Taxa	*Arbutus unedo*	*Betula* sp.	*Clematis* sp.	*Erica* sp.	cf. *Erica* sp.	Ericaceae	Fabaceae tp. *Genista*	Fabaceae tp. *Ulex*	Fabaceae	Pomoideae	Prunus sp.	cf. *Pteridium aquilinum*	deciduous *Quercus*	*Quercus* sp.	Indeterminable	Species minimal N.	Total
22				7	3	2	17		3				9		8	3	49
23	3		4	11			8		1				18		5	5	50
24			1	18	1		24		2	1			6		6	5	59
26		1		24			5	1	4				8		7	5	50
27	3		1	17	3		4	2	1	1			28		7	7	67
28				28		1	11		2				9		9	3	60
29				56			7	1	4				5		7	4	80
30				58	2	2	10		4	1			5	1	17	4	100
31	2			32	2		7		5	1			7		13	5	69
32	3			24	1	1	2		2				5		12	4	50
33	2			14	1		10		1				4		6	4	38
34	16			9			6						14		5	4	50
35	17			7		1	8		2				18		7	4	60
36	16	2		2			10					1	17	1	5	5	54
37	16						11		4				16		3	3	50
38	7						6		1				18	1		3	33
39	3						8	1					13	2		4	27
40							17		1				26		3	2	47
41							14						46			2	60
42							24						7			2	31

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MANUSCRIPT 8

Long-term deforestation in NW Spain: Linking the Holocene fire history to vegetation change and human activities.

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Long-term deforestation in NW Spain: linking the Holocene fire history to vegetation change and human activities

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ABSTRACT

The Holocene fire regime is thought to have had a key role in deforestation and shrubland expansion in Galicia (NW Spain) but the contribution of past societies to vegetation burning remains poorly understood. This may be, in part, due to the fact that detailed fire records from areas in close proximity to archaeological sites are scarce. To fill this gap, we performed charcoal analysis in five colluvial soils from an archaeological area (Campo Lameiro) and compared the results to earlier studies from this area and palaeo-ecological literature from NW Spain. This analysis allowed for the reconstruction of the vegetation and fire dynamics in the area during the last ca 11 000 yrs. In the Early Holocene, Fabaceae and *Betula* sp. were dominant in the charcoal record. *Quercus* sp. started to replace these species around 10 000 cal BP, forming a deciduous forest that prevailed during the Holocene Thermal Maximum until ~5500 cal BP. Following that, several cycles of potentially fire-induced forest regression with subsequent incomplete recovery eventually led to the formation of an open landscape dominated by shrubs (*Erica* sp. and Fabaceae). Major episodes of forest regression were (1) ~5500–5000 cal BP, which marks the mid-Holocene cooling after the Holocene Thermal Maximum, but also the period during which agropastoral activities in NW Spain became widespread, and (2) ~2000–1500 cal BP, which corresponds roughly to the end of the Roman Warm Period and the transition from the Roman to the Germanic period. The low degree of chronological precision, which is inherent in fire history reconstructions from colluvial soils, made it impossible to distinguish climatic from human-induced fires. Nonetheless, the abundance of synanthropic pollen indicators (e.g. *Plantago lanceolata* and *Urtica dioica*) since at least ~6000 cal BP strongly suggests that humans used fire to generate and maintain pasture.

1. Introduction

The elimination of forests is one of the most pervasive processes in landscape change in Europe during the Holocene (Kaplan et al., 2009). Fire was a major driver in deforestation and in the resulting formation and preservation of fire-adapted shrubland ecosystems, especially in the European Atlantic region (Conedera et al., 2009). Holocene fire regimes depended not only on climatic and biological factors, but also on ecosystem management by past societies. Human activity–fire–vegetation–climate interactions form a complex cycle of cause/stimulus and effect/response (Fábregas Valcarce et al., 2003; Vannière et al., 2008; Rius et al., 2009), because (i) climate and vegetation changes posed new opportunities and challenges to human groups and (ii) anthropogenic interference, which evolved with culture, needs and technological capabilities, produced both deliberate and unforeseen changes in the environment.

At present, in NW Spain shrub communities dominated by heathers (*Erica* spp.), gorse (*Ulex* spp.) and broom (mainly *Genista* spp. and *Cytisus* spp.) cover more than 25% of the surface. This shrubland is widely considered to be the product of recurrent burning (Santín et al., 2008) and 'traditional' slash-and-burn agricultural practices in particular (Bouhier, 1979; Balboa López, 1990). Some authors argued that the use of fire and the exploitation of shrub communities

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following the traditional scheme, well-documented in historical archives since the 17th century, was inherited from medieval times (1200–1500 AD) (Bouhier, 1979; Guitián Rivera, 2001; Criado Boado, in press). Less sophisticated fire-involved land clearance strategies most likely existed already in the Neolithic when agriculture arrived approximately 6500 yrs ago. Nonetheless, it is generally thought that before the Iron Age the anthropogenic impact to the landscape was relatively small (Van Mourik, 1986; Guitián Rivera, 2001; Muñoz Sobrino et al., 2001). However, due to a lack of fire history reconstructions, especially from the foci of past population in the coastal areas and inland basins (Ramil-Rego et al., 1998), the long-term dynamics of the fire regime and the resulting "fire landscape" and "fire culture" of NW Spain are only superficially understood.

The incomplete combustion of lignified plant tissues produces charcoal, of which the gross anatomical structure and most of its micro-structural elements resemble the structure of unburnt wood. Compared to other forms of organic matter, charcoal is resistant to abiotic and biological degradation (Forbes et al., 2006). Therefore, when preserved under appropriate conditions (Czimczik and Masiello, 2007; Braadbaart et al., 2009), it retains the original structure of the secondary xylem for thousands of years. The botanical identification of charcoal fragments on the basis of their anatomy (i.e. charcoal analysis, anthracology) can thus serve as an archaeological (indicating woodland exploitation) and palaeo-environmental (indicating woodland composition) proxy. Under favourable geomorphologic conditions, fire-driven vegetation succession can be recognised in the charcoal record of soils and sediments. Macroscopic charcoal analysis is often employed for 'on-site' archaeological contexts with limited timespan. However, anthracological studies of 'off-site' soil sequences, i.e. pedo-anthracology (Thinon, 1978) are less common, despite the fact that charcoal analysis represents one of the most powerful tools available for fire history research (Figueiral and Mosbrugger, 2000), combining direct evidence for the occurrence of local fires with the botanical identification of the burnt plant species.

The NW of the Iberian Peninsula harbours a type of colluvial Umbrisol traditionally referred to as Atlantic ranker. Such soils contain large amounts of organic matter (Carballas et al., 1967) and are the result of long-term (up to 15 000 yrs) erosion and sedimentation processes producing polycyclic soils composed of buried A horizons (Mücher et al., 1972). These colluvial soils form archives of Holocene environmental change (Kalis et al., 2003; Leopold and Völkell, 2007), even though colluvial processes often produce soils having a complex stratigraphy with chronological hiatuses and age inversions in the depth sequence. Recent studies on micromorphology and molecular composition of the soil organic matter have indicated that the colluvial soils of Campo Lameiro (NW Spain) are rich in biomass burning residues, including macroscopic charcoal (>2 mm) and smaller and often degraded ('humified') particles integrated into the fine fabric of the soil (Kaal and van Mourik, 2008; Kaal et al., 2008a). These studies raised a number of questions: to what extent was the vegetation pattern affected by the recurrent burning? And, what was the role of past societies in the fire regime?

This paper presents an anthracological study of five colluvial soil sequences from Campo Lameiro (NW Spain). The main objective is to reconstruct the Holocene fire history of the area from charcoal records. From that, we aim to build a chronological framework of fire history, climate change, vegetation change and human activities on a local scale, using earlier palynological, geomorphological and organo-geochemical characterisation studies from the area, as well as the available literature on vegetation and climate changes in NW Spain.

2. Regional setting

The study area is in the Rock Art Park of Campo Lameiro, on the upper part of the Monte Paradela hill (260–320 m a.s.l.), near the Paredes (PRD) parish in the municipality of Campo Lameiro (Pontevedra, NW Spain), at a distance of 25 km east of the Atlantic Ocean, in the Eurosiberian (Atlantic) phytogeographic region (Fig. 1). The parent rock is dominated by coarse granite of the Laxe group (IGME, 1982). Present climate is mild and humid: mean annual temperature is 15 °C and mean annual precipitation is 1200 mm (Martínez Cortizas and Pérez Alberti, 1999).

Campo Lameiro is well-known for its rock art (Bradley and Fábregas Valcarce, 1998; Santos Estévez, 2005), the majority of which were produced between ~4500 and 2500 cal BP, and is bound to become a major tourist attraction. Due to the scarcity of archaeological remains, the function of the area (ritual site, hunting ground, pasture, small-scale agricultural practices, nutrient/fuel source, etc.) and its changes through time remain to be investigated.

Current vegetation of the site is a mosaic of pine (*Pinus pinaster*), pedunculate oak (*Quercus robur*), heather (*Calluna vulgaris*), *Erica* spp. and herbaceous species. In 2003 and again in 2009, eucalyptus (*Eucalyptus globulus*) and shrub communities composed mainly of *Erica* spp., *Ulex* spp., *Cytisus* spp. and common bracken (*Pteridium aquilinum*), were eliminated (Rey García et al., 2004). After land expropriation in the early 2000s, animal husbandry and commercial forestry came to an end. Lower slopes surrounding the area are dominated by *Q. robur*, *P. pinaster* and *E. globulus*. Along the valleys, the riverside vegetation is mainly composed of common alder (*Alnus glutinosa*), hazel (*Corylus avellana*), *Q. robur* and birch (*Betula alba*). Cultivated land is located within a distance of 300 m of the study area, at lower elevations.

In the 'traditional' agropastoral system of NW Spain, a clear division can be made between land use at *el monte* (the upper slopes and low to mid-elevation mountain tops, such as the study area) and the valleys and lower slopes. Agricultural practices were concentrated in valleys and lower slopes. Two main approaches can be distinguished for land use at *el monte*. In the first approach, emphasis is on supplementary crop production following a slash-and-burn regime known as *roza* or *estivada*. In brief, shrub vegetation is cut/unrooted, dried in-situ, burnt, the ashes spread, the land cultivated and several years later abandoned to regenerate the soil under shrub vegetation, after which the cycle (10–15 yrs) is repeated (Bouhier, 1979; Balboa López, 1990). In the second approach, the shrubs themselves are exploited for fuel (wood/charcoal), livestock fodder or organic fertiliser (details in Balboa López, 1990). When used as organic fertiliser, the shrubs are implemented as stable bedding, after which the manure-enriched residues are applied to the cultivated soils in the valleys (e.g. Criado Boado, 1989; Bauer, 2005). The pivotal role of N-fixating Fabaceae shrubs, especially *Ulex europeaus*, in maintaining fertile cultivated soils is illustrated by the fact that their seed was actually sown (Bouhier, 1979). Moreover, *U. europeaus* shrubland was regularly rejuvenated by the use of fire to maintain monospecific shrub communities (*U. europeaus* is an efficient resprouter and germination of its seeds is stimulated by thermal shock; Reyes et al., 2009). Hence, in both approaches fire is a crucial element of recursive land clearance.

Vázquez de la Cueva et al. (2006) studied recent fire dynamics in Spain for the period 1974–2000. In this 26 year period, more than 500 fires were documented for the 10 × 10 km grid cell to which the study area belongs, being the highest fire activity for peninsular Spain (average 56 fires/grid cell; Gil-Romera et al., 2010). The combination of high intentionality (slash-and-burn and arson), high flammability of shrub and exotic tree communities, the abandonment of traditional land uses, high potential productivity (temperate climate) and dry periods during summer are the main causes of the exceptional fire activity in NW Spain nowadays (Balboa López, 1990; Carballas, 2003; Vázquez de la Cueva et al., 2006).

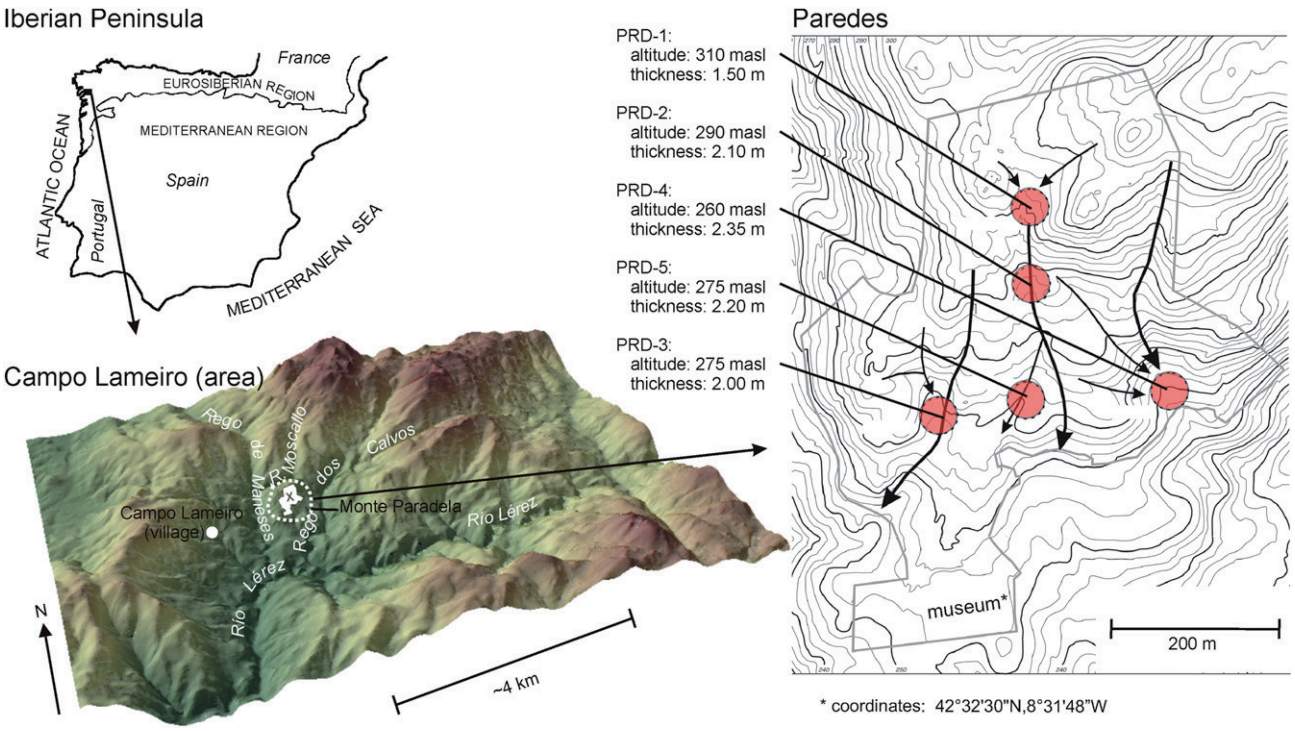

Fig. 1. Location of the study area and sampling sites (circles). Arrows in the topographical map reflect main sediment transport pathways.

3. Material and methods

Soil monoliths were taken from trenches in the PRD parish (Fig. 1). The soils were located in local depressions (alveoli). The monoliths were sliced into 5 cm sections. The material at the bottom of soil PRD-5 was too coarse for sampling. The elevation of the five soils, their thickness and the major sediment transport pathways are indicated in Fig. 1. Representations of soil profiles are combined with the results of charcoal analysis (Section 4.2).

Macroscopic charcoal was separated from the soil samples by wet-sieving through a 2 mm mesh-size sieve and weighed after drying (ca 24 h) to estimate charcoal concentration. The charcoal was botanically identified under a reflected light microscope by observing the three anatomical planes – transverse, radial longitudinal and tangential longitudinal – broken manually or with the aid of a razor blade. Anatomical features of charcoal fragments were compared to anatomical descriptions of European wood taxa (e.g. Schweingruber, 1990) and comparative wood and charcoal collections held in our host institutions. The proportion of charcoal from a given taxon is expressed as the percentage of the total number (not weight) of fragments analysed (Delhon, 2006). Unidentified charcoal was not included in the calculation. Pollen and charcoal records from one of the soils (PRD-2) were discussed by Carrión et al. (2010). The charcoal record of this soil is provided here as well for the sake of completeness.

Soil organic matter in the clay and silt fractions was obtained by wet-sieving soil samples through 50 μm, and submitted to Ångstrom Laboratory (Uppsala, Sweden) or Beta Analytic (Miami, USA) for acid–alkaline–acid extraction and AMS radiocarbon dating. Conventional ages were calibrated using Calib 6.0.1 (Stuiver and Reimer, 1993; Reimer et al., 2009) (Table 1). The radiocarbon age of charcoal from one sample of soil PRD-2 was similar to that of the soil organic matter from the same layer. Earlier studies suggested that the ages obtained are not biased by rejuvenation (Kaal et al., 2008b). Since the analysed soil profiles differed with regard to chronological resolution and timespan recorded, age estimations were needed for all samples in order to enable comparisons between them. The age of deposition was estimated from ^{14}C measurements, stratigraphic correlation of stone- and charcoal-rich layers, and, for the remaining samples, by linear interpolation between samples that were assigned an estimated age. Slope transport may have caused age inversion in the soils through the redistribution of old material on top of younger surfaces (Lang and Hönscheidt, 1999), which is one of the potential sources of inaccuracy in the age estimations. All ages referred to in this paper are in calibrated years before present (cal BP).

4. Results

4.1. General observations

Macroscopic charcoal was obtained from almost all samples (Fig. 2a–e). The soils exhibit different depth-curves for macroscopic charcoal content reflecting the complex geomorphology of the area and local differences in fire and vegetation history. The concentration of macroscopic charcoal is affected by many factors that are not mutually exclusive, such as fire type, fire intensity, post-depositional degradation, slope transport, vegetation composition, biomass availability and subsequent fires (e.g. Ohlson and Tryterud, 2000; Preston and Schmidt, 2006).

The vast majority of the charcoal fragments identified ($n = 4272$) originated from *Erica* sp. (34.4%), *Quercus* sp. (33.2%), Fabaceae (woody legumes, 23.0%) and *Arbutus unedo* (strawberry tree, 6.1%). In addition, *Betula* sp. (1.4%) and possibly *P. aquilinum* (0.73%) were frequent, and some fragments derived from *Clematis* sp. (0.42%), *Prunus* type (0.23%), Pomoideae (0.19%), *Berberis* sp. (0.09%), cf *Viburnum* sp. (0.02%), cf Asteraceae (0.02%), *Hedera helix* (common ivy, 0.02%) and *Pinus* sp. (0.02%). Most of the *Quercus* fragments were from deciduous oak (probably *Q. robur*). Based on pollen analysis, *Erica* sp. was mostly *Erica arborea* (tree heather) (Carrión et al., 2010).

Table 1
Results of radiocarbon measurements (AMS of acid–alkaline–acid extractable soil organic matter).

Soil	Depth (cm)	Material	^{14}C age BP	Calibrated age BP (2σ range)[a]	Laboratory code
PRD-1	50–55	Buried soil	2300 ± 40	2360–2155	Ua-21845
	70–75	Buried soil	3055 ± 40	3370–3160	Ua-21846
	90–95	Buried soil	5300 ± 50	6260–5940	Ua-21847
	125–130	Buried soil	7610 ± 55	8540–8340	Ua-21848
PRD-2	85–90	Buried soil	1835 ± 40	1875–1635	Ua-22555
	120–125	Buried soil	3055 ± 40	3370–3160	Ua-22556
	120–125	Charcoal	3125 ± 45	3380–3345	Ua-22559
	170–175	Buried soil	3770 ± 40	4285–3985	Ua-22557
	190–195	Buried soil	5350 ± 50	6270–6000	Ua-22558
PRD-3	50–55	Buried soil	4295 ± 35	4960–4825	Ua-34716
	115–120	Buried soil	4625 ± 35	5465–5295	Ua-34717
	160–165	Buried soil	4765 ± 40	5590–5330	Ua-34718
PRD-4	5–10	Buried soil	104.3 ± 0.4 pmC[b]	Actual	Ua-34719
	190–195	Buried soil	9760 ± 50	11 260–10 905	β-240963
PRD-5	35–40	Buried soil	840 ± 35	900–680	Ua-34720
	150–155	Buried soil	5635 ± 45	6495–6310	Ua-34721

[a] Calib 6.0.1 (Stuiver and Reimer, 1993; Reimer et al., 2009).
[b] Percent modern carbon.

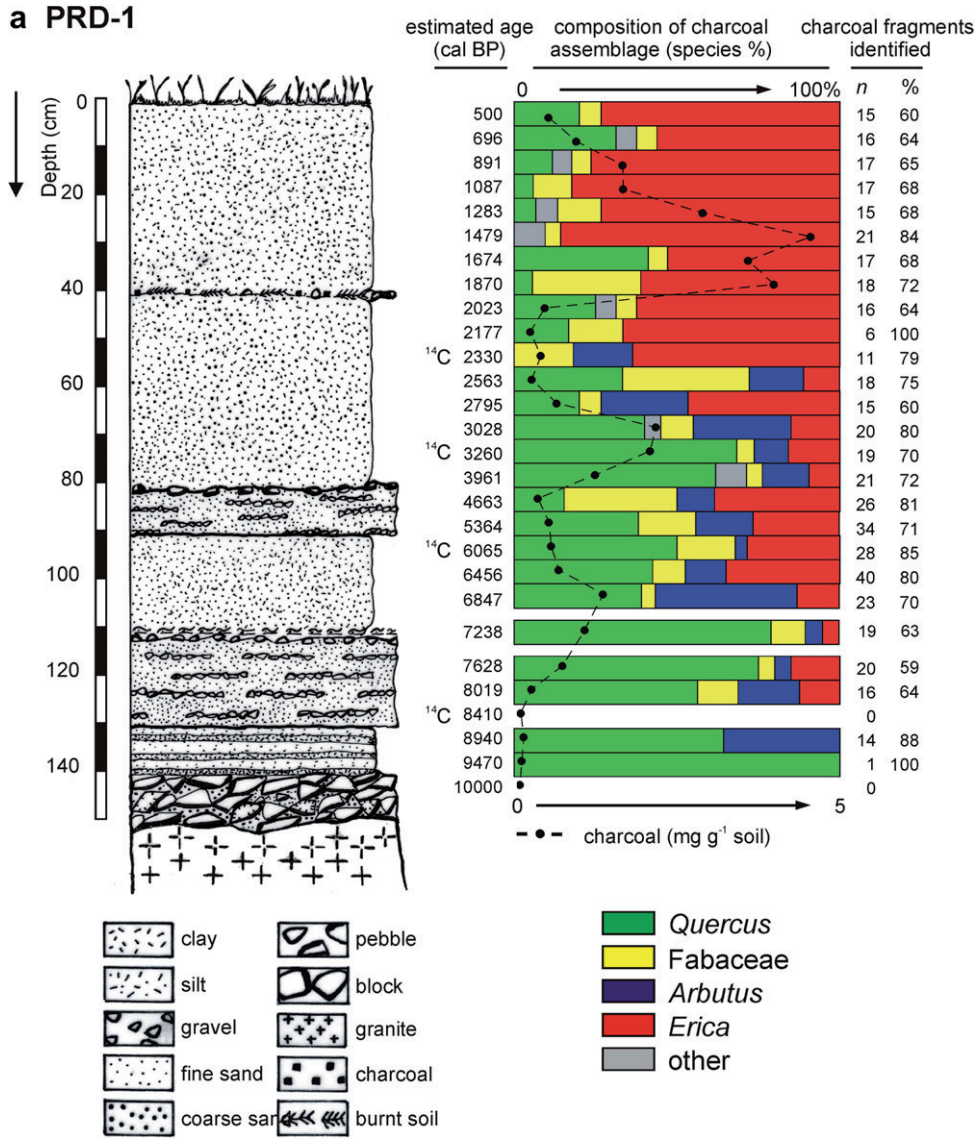

Fig. 2. Profile representations and results of charcoal analysis for *Quercus*, Fabaceae, *Arbutus*, *Erica* and others. The broken line represents macroscopic (>2 mm) charcoal content. Numbers to the right of the charcoal chart indicate the number of charcoal fragments identified (*n*) and the percentage of identifiable charcoal (%) from each sample.

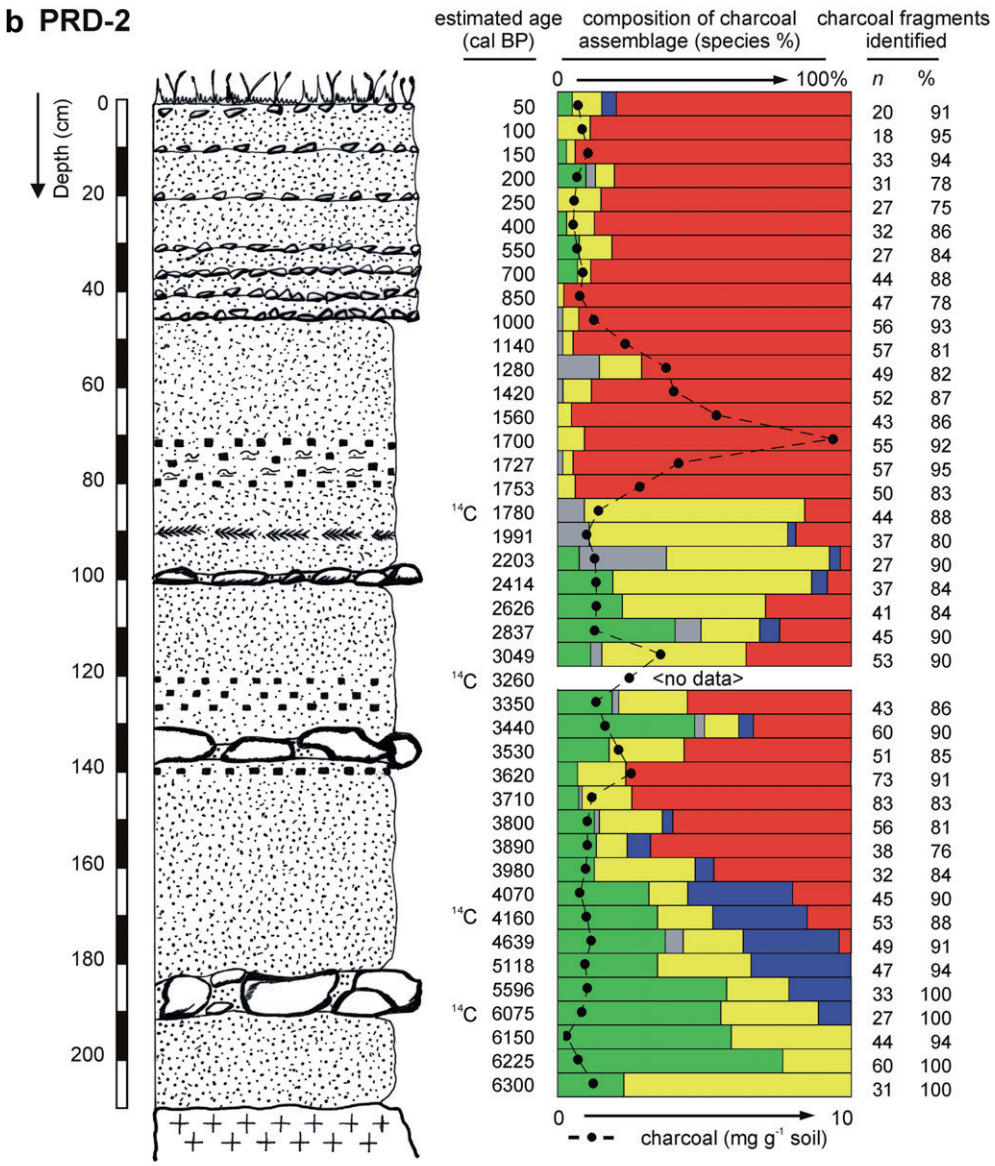

Fig. 2. (*continued*).

The Fabaceae family (Leguminosae) cannot be reliably identified at the genus level because their wood anatomy is extremely variable, even among individuals of the same species (Figueiral and Mosbrugger, 2000). Most of the dominant taxa in the charcoal records (*Q. robur*, *E. arborea*, *Betula* sp., *A. unedo*, *Ulex* sp., *Cytisus* sp. and *Genista* sp.) are capable of resprouting from roots, lignotubers, stumps or epicormic buds (Mesléard and Lepart, 1991; Paula and Pausas, 2008; Reyes and Casal, 2008), allowing them to rapidly colonise a burnt or otherwise disturbed area. Furthermore, the germination of the seeds of some of them, such as most Fabaceae shrubs in NW Spain, is stimulated by fire (Reyes et al., 2009).

4.2. PRD-1

No macroscopic charcoal was retrieved from the colluviated weathered saprolite at the bottom of soil PRD-1 (140–145 cm). The few fragments from the superimposed material, allegedly deposited between ~9500 and ~8500 cal BP (Costa Casais et al., 2009), were from *Quercus* sp. and *A. unedo* (Fig. 2a). *Quercus* sp. remained the dominant source until ~7000 cal BP. Then, a peak in macroscopic charcoal content coincided with a relative increase in *A. unedo* charcoal. Between ~7000 and ~3000 cal BP *Quercus* sp. is the dominant taxon but shrub species were also abundant. Around 3000 cal BP, a second peak in macroscopic charcoal content and a relative increase of *A. unedo* and later (before 2500 cal BP) *Erica* sp. and Fabaceae were observed. In the top half meter of the soil, with a layer of burnt material (at 40 cm depth) and a corresponding increase in macroscopic charcoal content, *Erica* sp. predominated.

4.3. PRD-2

Soil PRD-2 started accumulating around 6300 cal BP (Fig. 2b). The burnt vegetation was composed of Fabaceae and *Quercus* sp. A stone-rich layer at a depth of 180–190 cm may indicate severe erosion or might be a human artefact. This layer, dated to ~6000–5500 cal BP, is synchronous with a decline of *Quercus* sp. and a relative increase of *A. unedo* and, subsequently, of *Erica* sp. charcoal ~4000 cal BP. Between ~4000 and ~3500 cal BP burnt vegetation consisted for the most

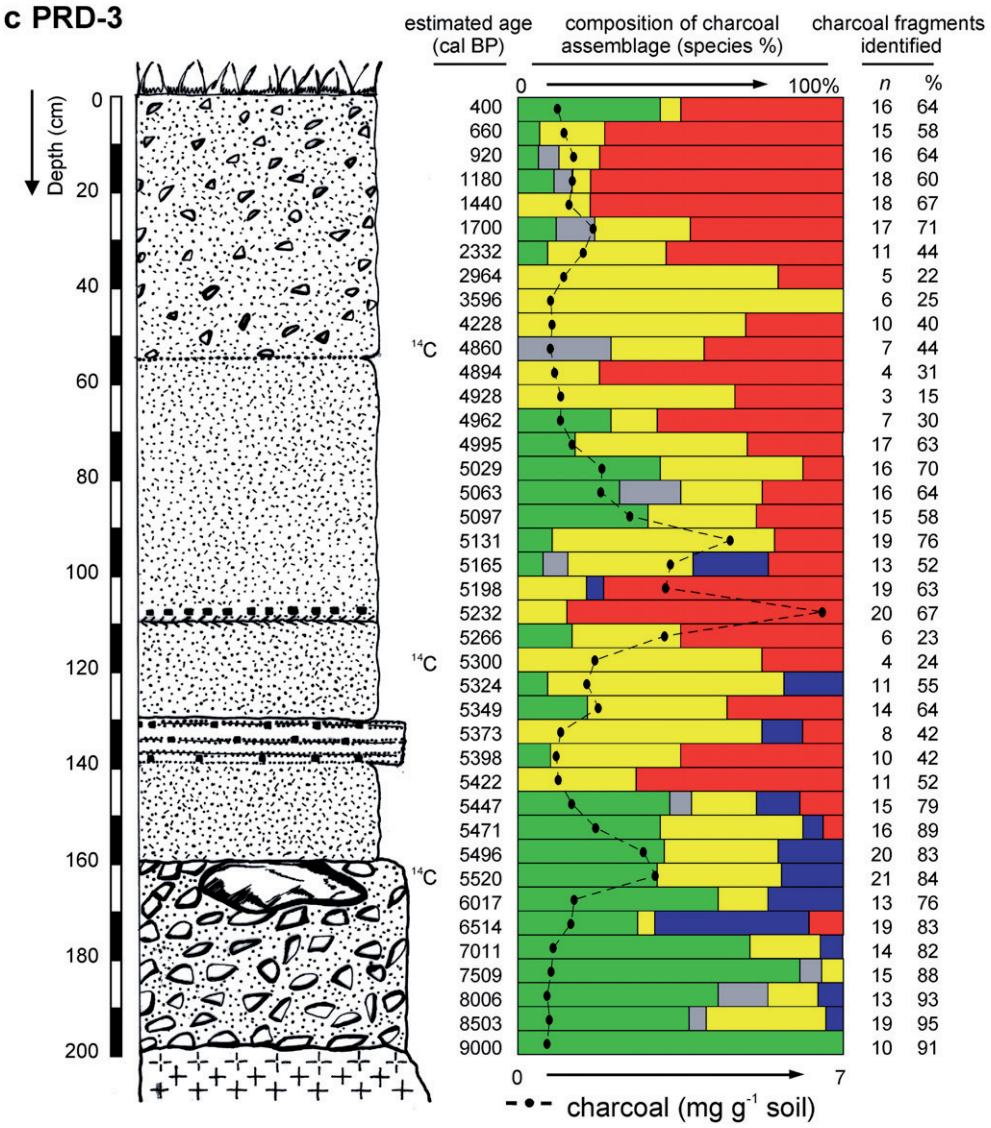

Fig. 2. (*continued*).

part of *Erica* sp. A small peak in macroscopic charcoal content at 140 cm (~3600 cal BP) represents a burning event that could have triggered heavy erosion resulting in the formation of a stone layer between 130 and 140 cm, although these stones may also be an archaeological artefact. This layer was followed by a decline in *Erica* sp. charcoal and an increase in the relative proportions of *Quercus* sp. and Fabaceae. Between ~3000 and ~1800 cal BP, the contribution of Fabaceae increased to 70% of the identified fragments. A drastic change in the composition of the burnt vegetation occurred ~1800 cal BP, when macroscopic charcoal concentration reached its highest level in the study area (almost 10 mg g^{-1} soil) and an abrupt increase of *Erica* sp. charcoal is observed. The upper layers of the soil maintained high *Erica* sp. percentages.

4.4. PRD-3

The base of the soil (160–200 cm) was rich in coarse material (Fig. 2c). The top of this layer was dated at 5590–5450 cal BP. Between ~9000 and ~6000 cal BP, most macroscopic charcoal fragments derived from *Quercus* sp. with smaller contributions of Fabaceae, *A. unedo* and *Betula* sp. The boundary with the superimposed finer soil material contained stones and a large amount of macroscopic charcoal (~5500 cal BP). During the following centuries (110–160 cm; 5500–5250 cal BP), *Quercus* sp. was replaced by Fabaceae and *Erica* sp. At about 5230 cal BP, the percentage of Fabaceae declined rapidly and *Erica* sp. became the dominant taxon, with a parallel increase in macroscopic charcoal content. Between ~5200 and 4860 cal BP macroscopic charcoal content gradually decreased and Fabaceae and *Quercus* sp. increased relative to *Erica* sp. Radiocarbon ages suggested that all material between 50 and 160 cm depth accumulated within 1000 years, starting between ~6000 and 5520 cal BP. A relatively large proportion of the charcoal fragments deposited between ~5000 and ~3000 cal BP was unidentifiable (Fig. 2c), thus generating unreliable data. The small peak in macroscopic charcoal content at 25–30 cm possibly corresponded to the major peaks found in PRD-1 and PRD-2, which coincided with an increase in *Erica* sp., replacing Fabaceae charcoal as the dominant taxon. At the surface, the contribution of *Quercus* sp. was relatively high.

4.5. PRD-4

The sample at 190–195 cm depth was dated 11 200 cal BP, suggesting that the bottom of soil PRD-4 (Fig. 2d) constitutes the

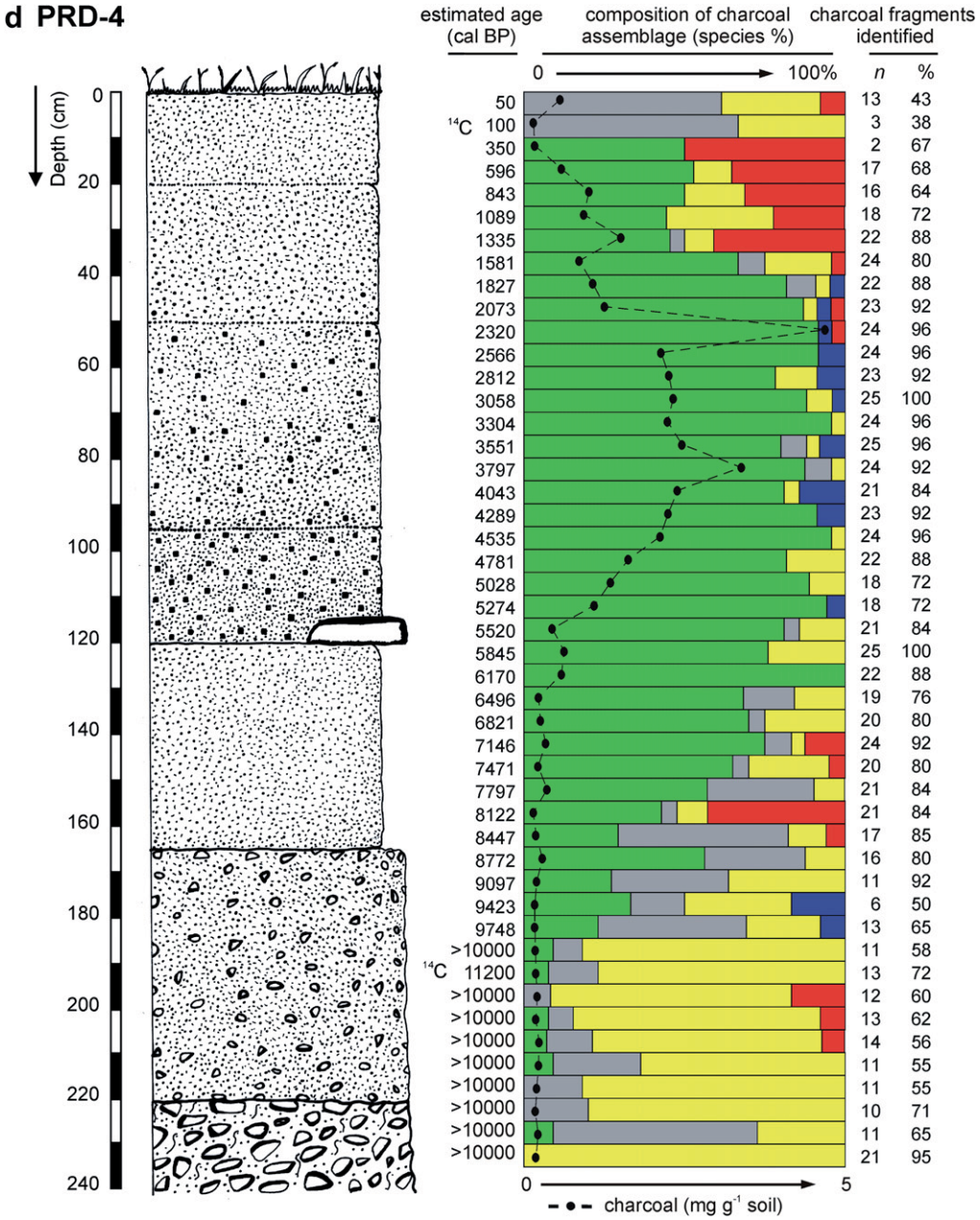

Fig. 2. (*continued*).

oldest dated material of the studied soils. The abundance of macroscopic charcoal from *Betula* sp. and absence of *Quercus* sp. in the bottom layers of this soil is consistent with this dating: during the Late Pleistocene/Early Holocene (~14 000–10 000 cal BP) *Betula* sp. was among the most ubiquitous tree taxa (Van Mourik, 1986; Muñoz Sobrino et al., 1997). At ~10 000 cal BP *Quercus* sp. began to substitute *Betula* sp. and Fabaceae, a process that was completed by ~7500 cal BP when *Quercus* sp. accounted for more than 70% of the macroscopic charcoal. Shortly after, *Betula* sp. charcoal disappeared completely. A stone-rich layer at 120 cm marks the onset of accumulation of macroscopic charcoal-rich material. Nonetheless, the macroscopic charcoal assemblage was dominated by *Quercus* sp. up until ~1600 cal BP. Then, Fabaceae and *Erica* sp. increased. The surface samples of PRD-4 probably contained macroscopic charcoal from glossy buckthorn (*Frangula alnus*). This is probably the youngest material studied here (Kaal and van Mourik, 2008; Kaal et al., 2008c).

4.6. PRD-5

The smallest amount of macroscopic charcoal was recovered from soil PRD-5 (Fig. 2e). This soil was located at a position subjected to high-energy slope dynamics, where coarse material was periodically deposited (and probably also removed). Until ~7000 cal BP, virtually all macroscopic charcoal was derived from *Quercus* sp. Subsequently the contribution of Fabaceae increased. Around 5500 cal BP, an additional sharp increase of *A. unedo* suggests further forest cover replacement by shrub vegetation, with a synchronous increase in macroscopic charcoal content. Between ~5500 and 1700 cal BP, most macroscopic charcoal was derived from Fabaceae.

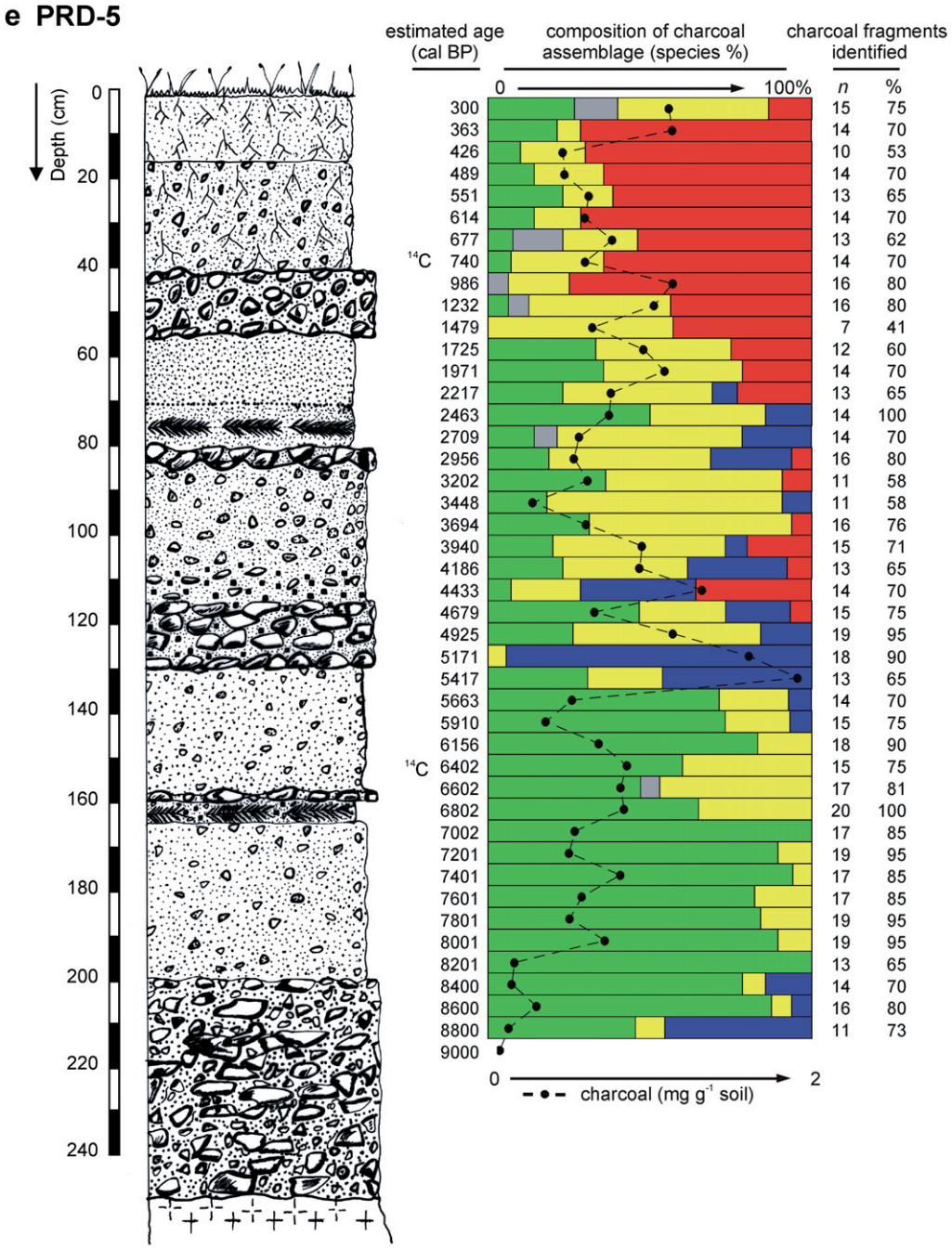

Fig. 2. (*continued*).

An increase of *Erica* sp. relative to Fabaceae and *Quercus* sp. began ~2200 cal BP but intensified ~1500 and ~1000 cal BP.

4.7. Charcoal records combined

The results of charcoal analysis of all samples from which 10 or more fragments could be identified ($n = 183$) are plotted against their estimated age in Fig. 3. The samples were clustered in age intervals of 500 yrs thereby eliminating some of the noise related to the inaccuracy in age estimations and probably the bias introduced by the sometimes limited number of identified charcoal fragments.

Before ~10 000 cal BP, macroscopic charcoal was mostly derived from *Betula* sp. (included in "other species" in Fig. 3) and Fabaceae. Then, *Quercus* sp. increased rapidly to almost 80% around 9000–8500 cal BP. *Quercus* sp. remained the dominant taxon until ~5500 cal BP, despite a decrease at ~7000–6500 cal BP when *A. unedo* and Fabaceae increased. Between ~5500 and 5000 cal BP, the contribution of *Quercus* sp. diminished. This coincided with a major peak in macroscopic charcoal content, the deposition of stones in PRD-2, PRD-3 and PRD-4, and an increase in the contribution of *Erica* sp. Between 4500 and 4000 cal BP, *Quercus* sp. had only partially recovered. A new episode of increased *Erica* sp. contribution occurred ~4000–3500 cal BP replacing *Quercus* sp. and *A. unedo*, an event that corresponded to a small increase in macroscopic charcoal content and a layer of stone-rich material in PRD-2. Following that *Quercus* sp. recovered towards 50% by

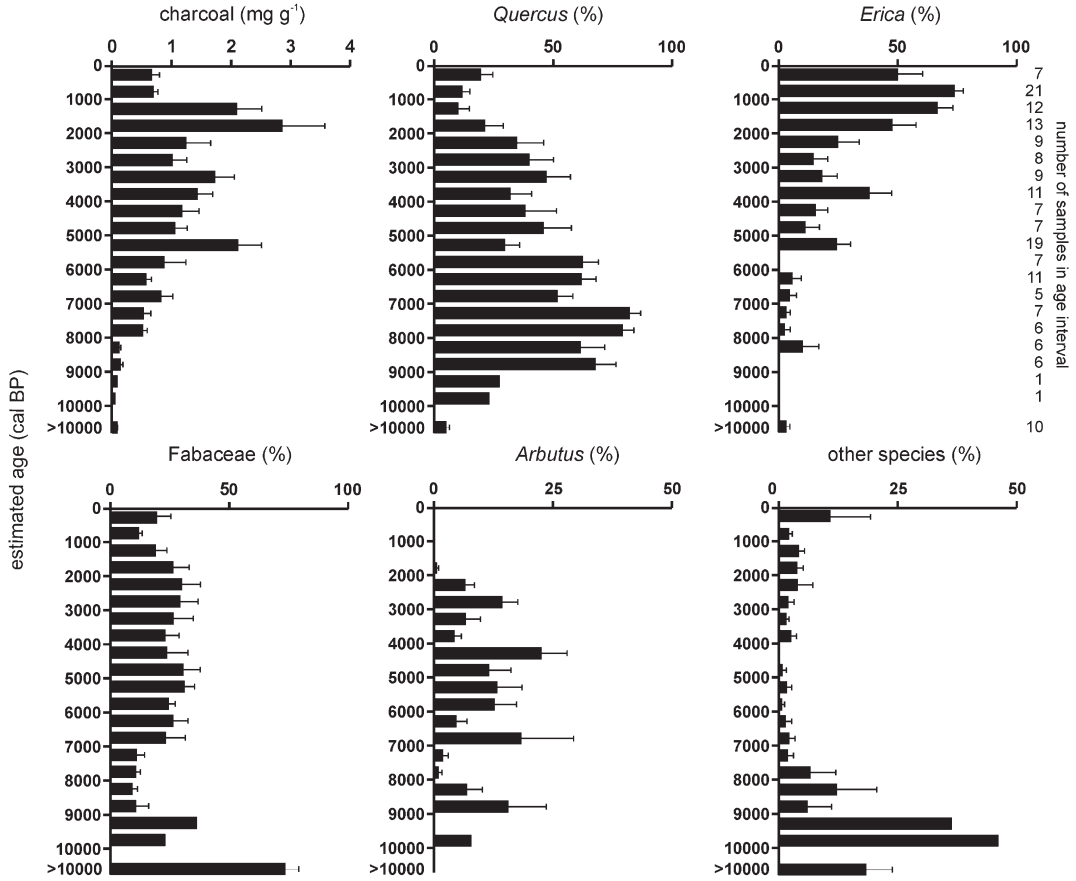

Fig. 3. Macroscopic (>2 mm) charcoal content and the relative contributions of the major taxa identified from the charcoal assemblages, after combining the data from the five soils and clustering in 500 yr intervals. The number of samples in each interval is indicated to the right. Error bars represent SEM of the samples in each interval. Most charcoal from "other species" before 7500 cal BP is *Betula sp.*

~3500–3000 cal BP. Between ~3000 and ~2000 cal BP, *Erica* sp. increased relative to *Quercus* sp. and *A. unedo* disappeared from the record. The replacement of oak by *Erica* sp. accelerated ~2000–1500 cal BP, when in many soils a macroscopic charcoal-rich layer was formed. The replacement of *Quercus* sp. by *Erica* sp. was almost complete around 1000 cal BP, when *Quercus* sp. and Fabaceae accounted for only 10% whilst *Erica* sp. accounted for 80% of the macroscopic charcoal. More recently (age estimations uncertain), the proportion of *Erica* sp. decreased while *Quercus* sp. and Fabaceae increased.

5. Discussion

5.1. Methodological considerations

Some methodological aspects are considered in order to establish the reliability of the proposed pedo-anthracological reconstructions. First, the number of identified taxa per sample was rather low. In the present study, three groups accounted for 89 ± 15% of the identified macroscopic charcoal fragments (*Quercus* sp., *Erica* sp. and Fabaceae). Pedo-anthracological assemblages derive from local fires fuelled by few different species and therefore require less than the 100–500 fragments per sample recommended for the analysis of assemblages derived from 'on-site' archaeological contexts (Tardy, 1998; Carrión, 2005). A relatively large amount of macroscopic charcoal fragments was used for PRD-2, but the taxonomic diversity was still low (Carrión et al., 2010). Therefore, the data obtained were expected to be representative of the macroscopic charcoal assemblages. Nonetheless, the small fragment number does imply that only the dominant species are recorded (Delhon, 2006).

Second, a macroscopic charcoal assemblage is not representative of the full spectrum of species present in past vegetation. Non-woody plants (grasses, sedges and ferns) are often not preserved or their charred remains are too small to be identified. Also, species with relatively soft wood, such as *Pinus* sp. and *Betula* sp., tend to conflagrate faster and reduce to ashes more easily than denser woods such as *Erica* sp. and *Quercus* sp. (Rossen and Olson, 1985; Scott et al., 2000). As a result, some species may be under-represented and others over-represented. Nonetheless, significant variations in taxon representation usually reflect changes in the vegetation community.

Third, charcoal may lose specific anatomical features e.g. due to vitrification, shrinkage, cracking and post-depositional physical and biological degradation whereby especially small fragments may become unidentifiable (Braadbaart et al., 2009), thus producing additional biases. In the present study, 22 ± 7% of the macroscopic charcoal fragments analysed could not be identified due to these processes, as well as the abundance of fragments of small twigs. The percentage of indeterminate charcoal fragments did not increase significantly with depth/age. Three periods had higher than average counts of indeterminate charcoal, viz. ~1000 cal BP-present, ~5500–4500 cal BP and >10 000 cal BP. The percentage of indeterminate charcoal was inversely related to the contribution of *Quercus* sp. ($r^2 = 0.35$; $P < 0.001$): *Quercus* sp. is relatively easily recognised creating a positive identification bias for this taxon. *Quercus* sp. contributions can thus be expected to be somewhat overestimated.

Finally, the provenance of the macroscopic charcoal fragments has to be viewed in the light of slope processes. Aeolian transport or convectional uplift of charcoal fragments >2 mm is very unlikely (Blackford, 2000). Thus, all macroscopic charcoal fragments formed on the hill studied. Considering the evidence for the redistribution of gravel and stones in the area, waterborne transport of macroscopic charcoal is more likely (Forbes et al., 2006). Differences in sedimentation rate of soil material and macroscopic charcoal affect the temporal and spatial resolution of the records studied, and also produce bias in the dataset obtained by combining the soils.

These problems related to the representativeness of the macroscopic charcoal assemblages in combination with the difficulties in obtaining reliable chronologies are inherent to fire history reconstructions from colluvial soils. However, studying fire prone biomes that are not connected to local well-stratified lake, pond or peat deposits relies on the archives from such deposits. The key is to focus on the major changes detected and accept that the ages assigned are estimations.

5.2. Chronological framework of fire history, vegetation change, climate change and human activities

Figs. 3 and 4 represent the major changes in woody vegetation during the last ~10 000 years, based on the macroscopic charcoal records. In Fig. 4, ten tree or shrub symbols are depicted at each of the sites. Each symbol represents 10% of the identified macroscopic charcoal for a given period. Table 2 summarises climatic change, cultural shifts and changes in the macroscopic charcoal and pollen records in NW Spain for the last 10 000 yrs.

5.2.1. Before 10 000 cal BP: Early Holocene open landscape

Before ~10 000 cal BP, the woody vegetation was probably a mixture of *Betula* sp. and Fabaceae. Palynological studies in NW Spain have shown that the vegetation of the Late Pleistocene/Early Holocene was dominated by grasses in an open landscape (Santos et al., 2000; Muñoz Sobrino et al., 2001) that may be considered as steppe vegetation (Van Mourik, 1986). Although the contribution of herbaceous plants is missing from the macroscopic charcoal record, the presence of the light-demanding Fabaceae and *Betula* sp. is consistent with thin canopy. In NW Spain, *Betula* sp. was especially important in the coastal and sub-coastal areas under oceanic conditions, while in the mountainous and inland regions this role was assumed by *Pinus* sp. (e.g. Muñoz Sobrino et al., 2004). It is unlikely that the hunter–gatherer societies of the Palaeolithic exerted significant influence on the vegetation during this period.

5.2.2. 10 000–8000 cal BP: colonisation by oak

A rapid expansion of *Quercus* sp. occurred around 10 000 cal BP (Fig. 3). Some *Betula* sp. is still observed on the lower sites of the area (PRD-3 and PRD-4; Fig. 4) where the higher water table and lower

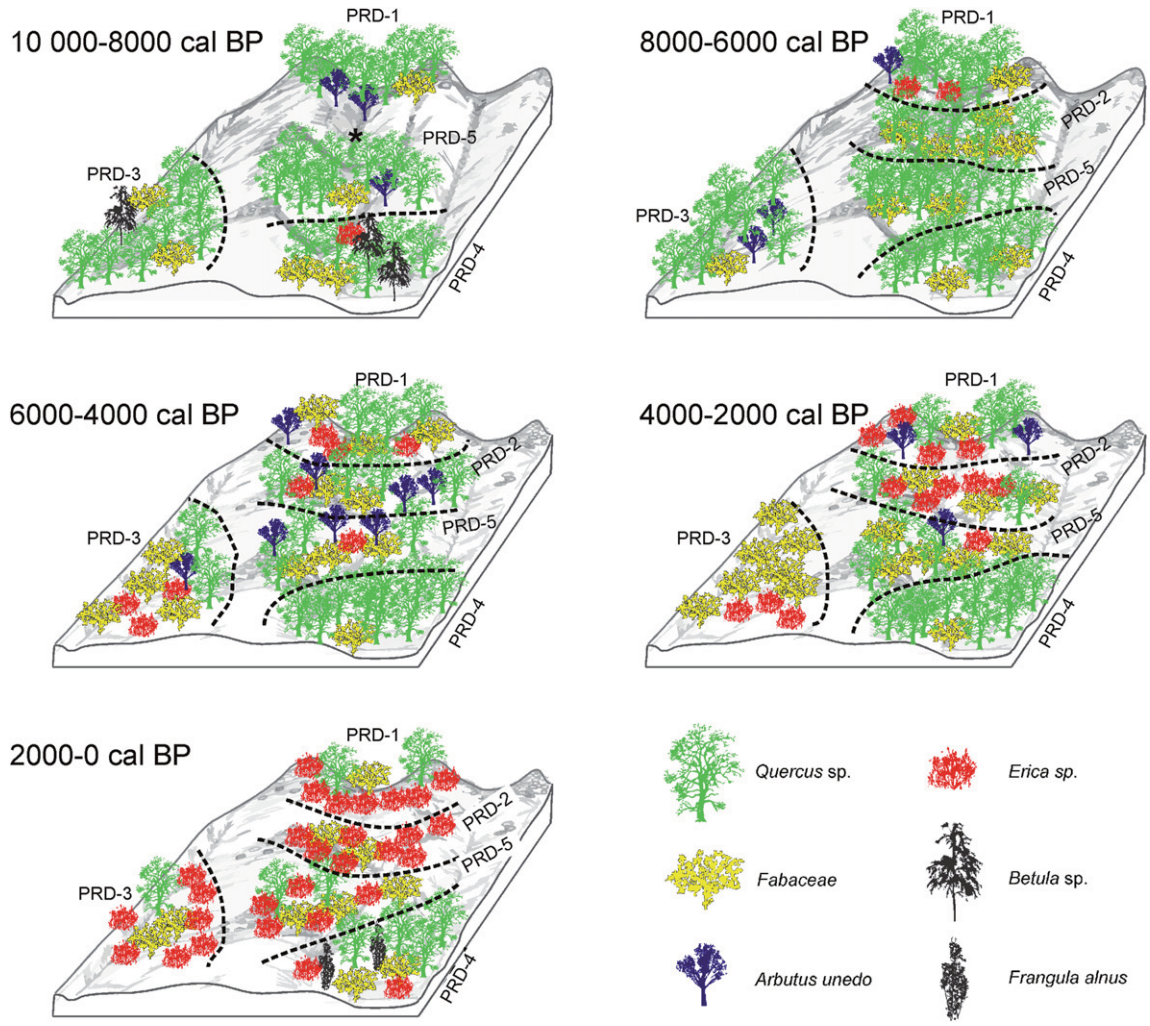

Fig. 4. Vegetation change in time and space. For each period and site, ten shrub/tree symbols are depicted, each of which represents 10% of the average composition of the charcoal assemblages of that period and on that site. * = no data available for PRD-2 between 10 000 and 8000 cal BP.

Table 2
Summary of Holocene climate, vegetation (from pollen and charcoal) and cultural events in NW Spain.

Chronology cal BP	Climatological sequence	Pollen sequence	Charcoal sequence (this study)	Cultural sequence
Before 10000	Lateglacial-Early Holocene climate fluctuations. Cold and generally dry conditions.	Steppe-like vegetation consisting of Poaceae, *Artemisia, Pinus, Betula* and Fabaceae.	*Betula*-Fabaceae dominance. Low macroscopic charcoal content.	Upper-Palaeolithic. (Magdalenian) hunter–gatherers.
10 000–8000	Early Holocene climate amelioration. 8.2 ka severe dry spell.	*Quercus* expansion. Short-lived forest regression (8.2 ka event).	*Quercus* expansion. *Betula* and Fabaceae decrease.	Mesolithic/Epi-palaeolithic hunter–gatherers.
8000–6000	Holocene Thermal Maximum. Wet and warm conditions.	Deciduous *Quercetum mixtum* assemblage (mainly *Q. robur, Alnus, Betula* and *Corylus*).	*Quercus* dominance. Increase in macroscopic charcoal content. *Arbutus* peak and forest retreat 7000–6500 cal BP. *Betula* disappears.	Mesolithic-Early Neolithic. Woodland clearance (fire) for hunting. Incipient agriculture from ~6500 cal BP.
6000–4000	Climate deterioration (colder, drier, windier). Cold spells and strong fluctuations in humidity ~5000 and ~4200–3800 cal BP.	Forest retreat and shrubland expansion. Disturbance indicators (*Plantago, Urtica, Sordaria*) abundant, decrease in *Quercus*, increase in grasses.	*Quercus* decreases and *Erica-Arbutus* increases. Peak in macroscopic charcoal content.	Neolithic/Early Bronze Age. Generalisation of agriculture and animal husbandry. Funerary megaliths. First petroglyphs in study area.
4000–2000	~4200–3800 cal BP dry event? ~3500 cal BP climate amelioration: increase in temperature and humidity. Short-lived cool and wet phase ~2700 cal BP.	Continued forest regression and shrubland expansion. *Plantago, Urtica* and *Sporormiella* as grazing disturbance indicators in the study area. Cereal cultivation in Campo Lameiro.	Small perturbations: *Erica* high, *Quercus* low, Fabaceae abundant. Macroscopic charcoal content remains high.	Bronze Age–Iron Age. Most rock art in study area. Bell beaker pottery. Castro Culture. Migration towards valleys.
2000–0	Roman Warm Period followed by climate deterioration, the Medieval Warm Period, the little ice age and actual global warming.	Definitive expansion of *Erica*. Minor presence of cereal type pollen and *Castanea* in study area. *Pinus* afforestation during last few centuries.	Establishment of mature *Erica* communities. *Quercus* minimum values. Peak in macroscopic charcoal content.	Romanisation, Germanic Period, maturation of traditional rural system.

susceptibility to fire might have favoured *Betula* sp. This period saw a swift colonisation of NW Spain by *Q. robur*, especially in the Atlantic region, owing to climatic amelioration between 10 000 and 8000 cal BP (Ramil-Rego et al., 1998). The onset of *Quercus* sp. expansion by ~10 000 cal BP is in agreement with earlier palaeoecological records (e.g. Santos et al., 2000; Carrión, 2003). Fabaceae and *A. unedo* represent subordinate shrub communities. The fire regime was not intense enough to cause a serious decline in forest cover. Whether those fires were prompted by natural causes or by hunter–gatherers is unknown, but a significant anthropisation of the landscape before 8000 cal BP is not supported by literature from the region (Martínez-Cortizas et al., 2009). Erosion was limited under the relatively stable conditions that prevailed during this period (Costa Casais et al., 2009). A small increase in the proportion of *Erica* sp. charcoal and decrease in *Quercus* sp. around 8500–8000 cal BP might reflect the short-lived cold and dry spell around 8200 cal BP (the 8.2 ka event) (Mayewski et al., 2004; Martínez-Cortizas et al., 2009).

5.2.3. 8000–6000 cal BP: stabilisation of oak forest

The charcoal assemblages from this period were dominated by *Quercus* sp. (Figs. 3 and 4). Many records from NW Spain have shown that the *Quercus*-dominated forest cover was at its maximum between 8500 and 6500 cal BP (Gómez-Orellana et al., 1998; Gómez-Orellana, 2002; Carrión, 2005) under the favourable (warm and wet) climatic conditions of the Holocene Thermal Maximum. The forest optimum was possibly interrupted by a phase of forest retreat ~7000–6500 cal BP. The simultaneous increase in macroscopic charcoal content (Fig. 3) suggests that an intensified fire regime was associated with this vegetation perturbation, which is also reflected in pollen sequences that are in close vicinity of settlements (Ramil-Rego et al., 2001). There is no evidence of climatic change that could explain this event. It remains unclear whether human activities (e.g. woodland clearance for hunting purposes and early pastoral activities) were associated with the Epipalaeolithic/Mesolithic fire regimes in Europe (Carcaillet et al., 2002).

5.2.4. 6000–4000 cal BP: Neolithic episode of oak forest degradation

Multiple indicators from the study area point towards profound landscape alteration around ~5500 cal BP. (1) Accelerated erosion is reflected by stone-rich layers and rapid soil accumulation at PRD-3 (details in Costa Casais et al., 2009). (2) A simultaneous peak in macroscopic charcoal content (Fig. 3) suggests that erosion was aggravated by fire. (3) The soil reaction in water (pH) decreased abruptly from 5.2 to 4.6 (Kaal et al., 2008c). (4) Molecular characterisation of the organic matter suggested a change in fuel source and/or fire intensity (Kaal et al., 2008b). (5) The contribution of *Quercus* sp. charcoal decreased while *Erica* sp. increased (Figs. 3 and 4). This was not the case at PRD-4 though, probably because it is located at a lower elevation. (6) Herbaceous pollen showed a sharp increase relative to *Quercus* sp., suggesting a reduction of forest canopy (Carrión et al., 2010). (7) The presence of synanthropic pollen indicators (e.g. *Plantago lanceolata* and *Urtica dioica*) from ~6000 cal BP onwards (Carrión et al., 2010) suggests that humans used fire to clear the land, probably to facilitate animal grazing (Behre, 1981; López Sáez et al., 2003a). The combination of fires, grazing disturbance and soil degradation would have promoted the expansion of *E. arborea* because of the efficient post-disturbance resprouting ability (Mesléard and Lepart, 1989; Riba, 1998) and its capacity to obtain nutrients from resource poor environments through mycorrhizal roots (Bergero et al., 2000). Similarly, at Mougás, located 60 km from the study area, *Quercus* sp. was replaced by *Erica* sp. and Fabaceae approximately 6000–5500 cal BP (Gómez-Orellana, 2002) and in central/north Portugal pasture was created by fire ~6000 cal BP (Rochette Cordeiro, 1992; Van der Knaap and van Leeuwen, 1995). Elsewhere in NW Spain, cereal pollen and non-pollen palymorphs related to grazing disturbance were recorded roughly since 6000 cal BP (Ramil-Rego and Aira Rodríguez, 1993; Ramil-Rego et al., 1994; Mighall et al., 2006). Meanwhile, accelerated erosion became a widespread phenomenon which has been linked to human activity (Martínez Cortizas et al., 2000, 2005, 2009).

It is generally accepted that anthropogenic deforestation for pasture and agricultural fields caused a major reconfiguration of the European landscape ~6000 cal BP (Clark et al., 1989; Carcaillet et al., 2002; Tinner et al., 2005; Hajdas et al., 2007), but for NW Spain this event is often less explicit than the deforestation phases that occurred later (e.g. Van Mourik 1986; Guitián Rivera, 2001; Ramil-Rego et al., 2001). On the other hand, this phase roughly coincides with the mid-Holocene climate transition, i.e. the onset of "neoglaciation", around 5600–5300 cal BP in Central Europe (Magny et al., 2006) and approximately 5000 cal BP in NW Spain (Luque Marín, 2003; Mighall et al., 2006). Temperatures were between 2 and 2.5 °C lower than today, which meant a cooling trend of ~4–5 °C relative to the Holocene Thermal Maximum (Martínez Cortizas and Pérez Alberti, 1999, 2009). Temperature records from the Penido Vello peat bog in NW Spain suggested low temperatures until ~3500 cal BP (Martínez Cortizas and Pérez Alberti, 1999). In NW Spain, the term "neoglaciation" is sometimes used as the period between 5000 and 3500 cal BP as a prolonged cold period with strong fluctuations in humidity (Martínez Cortizas and Pérez Alberti, 1999; Mighall et al., 2006; López-Merino et al., 2010). The return to cold conditions ~5000 cal BP may explain accelerated erosion and forest retreat, but it is unlikely that it produced an intensification of the burning regime and an increase in synanthropic pollen indicators. A combination of increased landscape fragility due to climatic change and an adaptation and/or intensification of human activities may well explain why this is one of the strongest pre-industrial episodes of Holocene environmental change (Fábregas Valcarce et al., 2003; Magny et al., 2006; Martínez-Cortizas et al., 2009).

Between ~5000 and ~4000 cal BP macroscopic charcoal content decreased but remained higher than before ~5500 cal BP. The proportion of *Quercus*-derived charcoal increased but remained below its Holocene Thermal Maximum levels, suggesting partial recovery of the forest. Fire combined with continued grazing disturbance (Carrión et al., 2010) probably inhibited further development of deciduous *Quercus* sp. woodland.

5.2.5. 4000–2000 BP: Bronze Age/Iron Age episodes of environmental change

A small increase in macroscopic charcoal content, the second peak of *Erica*-derived charcoal and a minimum in the proportion of *Quercus* sp. (Fig. 3) suggest that approximately 4000–3500 cal BP the fire regime intensified again. High-altitude lacustrine sediments in NW Spain showed evidence of regression of *Quercus* sp., which may be anthropogenic (Muñoz Sobrino et al., 2001) but also related to a cold and dry phase ("the 4.2 ka event") between 4200 and 3800 cal BP (Booth et al., 2005; Magny et al., 2009). This period (the Early Bronze Age) is not often identified as a phase of major human-induced environmental change (Martínez-Cortizas et al., 2009). The presence of *Sporormiella* type (T113), *Urtica* and *Plantago* (but no Cerealia) point towards continued grazing disturbance and the consolidation of the agropastoral system. The decrease in *A. unedo* contribution may reflect climate change. Maybe the climatic effect exacerbated the impact of fire and grazing on the composition of the shrubland (*Erica* sp. vs *A. unedo*) even though land use practices did not change significantly.

After ~3500 cal BP, the contribution of *Quercus* sp. increased towards 50% of the identified charcoal and *Erica* sp. decreased, despite the high concentration of macroscopic charcoal. The slight *Quercus* sp. recovery in spite of recurrent fires may be explained by the increase in humidity in NW Spain from ~3600 cal BP until ~3000 cal BP (Fábregas Valcarce et al., 2003; Mighall et al., 2006).

Between ~3000 and ~2000 cal BP, the proportion of *Quercus* sp. charcoal decreased slightly. The charcoal from the shrub communities originated from Fabaceae, *Erica* sp. and *A. unedo*. Martínez Cortizas et al. (2005, 2009) inferred that deforestation, soil acidification and accumulation of heavy metals, such as lead, in peat records accelerated since ~3000 cal BP, which marks the transition between the Late Bronze Age and the Iron Age. This transition is characterised by a series of technological and economic changes that included the development of a substantially more complex agrarian productive system, an increase in mining activities and the production of metallic objects – of bronze and also iron at later stages – which undoubtedly resulted in increased fuel demand (Martín Seijo, 2006) and which allowed for artificial drainage and therefore cultivation of the wet and relatively clay-rich soils in the valleys (López-Sáez et al., 2003b; Criado Boado, in press). In the coastal regions of NW Spain woodland and forest vegetation were largely replaced by Ericaceae and Fabaceae shrublands due to the concentration of human settlement in these areas. It also coincided with unequivocal evidence of human activities in the form of pollen and non-pollen palynomorphs that are associated with pastoral and agricultural activities, also in the Campo Lameiro area (Aira Rodríguez et al., 1990; Carrión et al., 2010). Although this period may be characterised by mild climatic conditions, it includes the "2.8 ka event" (Van Geel et al., 1996; Alley et al., 1997; Speranza et al., 2002), which was reflected by an intensified storm regime and a return to cooler and wetter conditions in NW Spain (Martínez Cortizas and Pérez Alberti, 1999; González-Álvarez et al., 2005; Mighall et al., 2006). Around 2500 cal BP, temperatures and humidity started to increase again, culminating in the Roman Warm Period (2200–1700 cal BP) (Holzhauser et al., 2005; Carrión et al., in press). Climate amelioration after the 2.8 ka event was not reflected in the charcoal record by an increase in *Quercus* sp. charcoal but the pollen record did show a minimum in shrub-derived pollen and a maximum in *Alnus* sp. (Carrión et al., 2010), which may be associated with wetter conditions (Aira Rodríguez and Saá Otero, 1988). Perhaps local disturbance on the upper part of the hill (grazing, fire) inhibited forest expansion in the study area.

5.2.6. 2000-present: environmental change since the Roman/Germanic period

A peak in macroscopic charcoal content combined with a decline in *Quercus* sp. and its almost complete replacement by *Erica* sp. (>80%) are strong indicators of fire-related vegetation change at ~2000–1500 cal BP. Molecular characterisation of soil organic matter suggested that these were intense fires similar to those during the Holocene Thermal Maximum period (Kaal et al., 2008b). *A. unedo* disappeared from the area and Fabaceae were also partially replaced by *Erica* sp. The pollen record also shows a marked increase from 8 to 35% of *Erica* cf *E. arborea*, a decrease in the percentage of *Quercus* sp. while *Alnus* sp. diminished (Carrión et al., 2010). This phase, roughly corresponding to the Late Roman period and the transition to the Germanic period, may be associated with climate deterioration (end of the Roman Warm Period) and a profound shift in land use management (Ballesteros Arías, 2003). Climatic deterioration would have hampered vegetation recovery after fire and exacerbate human impact (deforestation) in general (Mighall et al., 2006), thereby triggering accelerated erosion (Martínez Cortizas et al., 2005), to which terrace building may have been a response (Ballesteros Arías, 2010). Afterwards, *Erica* sp. remained the dominant taxon in the studied area. Nonetheless, herbaceous pollen and charcoal concentrations decreased and a decline in the percentage of charcoal with strongly curved growth rings (Carrión et al., 2010) suggested that a mature *Erica* sp. shrubland had formed under reduced fire and grazing pressure (Pesqueira et al., 2005). A decrease in population with land abandonment may explain the expansion of shrubs relative to herbaceous species despite the weakened fire regime (Allen et al., 1996; Guitián Rivera, 2001). Forest regrowth was probably mitigated by the acidity of the soil surface as well ($pH\text{-}H_2O = 4.7 \pm 0.2$ ($n = 51$) for material deposited after ~1800 cal BP)

(Kaal et al., 2008c), so that species that cope well with such conditions through mycorrhizal associations remained competitive. However, fungi (Kaal and van Mourik, 2008) and their molecular markers (chitins) were not abundant (Kaal et al., 2008a). Signals from recent episodes of climatic change (Medieval Warm Period, Little Ice Age) were not reflected by the charcoal and pollen records because of the lack of samples from these periods or the signal overridden by land use management. Small concentrations (<2%) of cereal pollen were found in the layers between 20 and 50 cm of PRD-2 (Carrión et al., 2010), which is certainly after 1600 cal BP and probably after 1000 cal BP. This weak pollen signal cannot confirm or reject local cereal cultivation (López Sáez et al., 2003a). It may represent background noise derived from nearby areas surrounding the hill where agricultural practices are more pronounced (Aira Rodríguez et al., 1990). More recently, possibly in the course of the last few centuries, *Quercus*-derived charcoal and pollen increased slightly at the expense of *Erica* sp. A sharp increase in *Pinus* sp. pollen probably originates from recent plantations (Carrión et al., 2010).

5.3. Synthesis: deforestation and the origin of the cultural shrubland in NW Spain

The agreement with previous palaeo-ecological investigations suggests that the results of the present study can be of general application for NW Spain, and a synthesis can be made.

In the Early Holocene, deciduous *Quercus* sp. colonised NW Spain thereby forming a well-developed natural forest during the Holocene Thermal Maximum. A decrease in the contribution of *Quercus* sp. and increase in charcoal from *A. unedo* between ~7000–6500 cal BP might reflect an early phase of anthropogenic forest retreat. Since ~5500 cal BP, starting at higher elevations of the hills (Fig. 4), forest cover progressively declined as a result of climatic change, fire and grazing disturbance. The resulting soil erosion and sedimentation accompanied by the accumulation of burning residues culminated in the formation of black colluvial soils supporting disturbance-adapted shrubland. Such vegetation is ubiquitous on the upper slopes and flats of the abandoned hilly terrain (*el monte*) in present-day NW Spain, while valleys still harbour significant, albeit strongly fragmented, expanses of deciduous woodland.

The contribution of Fabaceae-derived charcoal does not respond strongly to the major deforestation cycles. The abundance of Fabaceae in the charcoal record seems to relate primarily to the amount of light that reaches the forest floor: large proportions in the Late Pleistocene/Early Holocene open woodland and the rapidly rejuvenating shrubland between 6000 and 2000 cal BP, and small proportions under the well-developed deciduous forest canopy of the Holocene Thermal Maximum and the dense *Erica* sp. formations since roughly 1500 cal BP. *Erica* sp. seems to be a better indicator of environmental degradation and deforestation: peaks in *Erica* sp. charcoal coincide with minima in *Quercus* sp. and the decline in *Quercus* sp. is, since 9000 cal BP, inversely related ($n = 171$, $r^2 = 0.55$, $P < 0.001$) to the increase in *Erica* sp., which is not the case for *A. unedo* or Fabaceae. Episodes of relatively severe change (increase in macroscopic charcoal content, minima in the proportion of *Quercus* sp. charcoal, maxima in *Erica* sp., soil acidification and erosion) occurred in the Neolithic (~5500–5000 cal BP) and in the Late Roman/Germanic period (~2000–1500 cal BP). Between ~5000 and ~2000 cal BP the equilibrium of the oak woodland/shrub communities was more or less stable, apart from two minor perturbations around ~4000–3500 cal BP and ~3000–2000 cal BP.

In comparison with the picture obtained from pollen and microscopic charcoal records in NW Spain, forest retreat during the Neolithic period suggested by the macroscopic charcoal record is much more pronounced (Van Mourik, 1986; Ramil-Rego et al., 2001). This might suggest that the study area was subjected to more intense human transformations by Neolithic societies. This idea is supported by the fact that in the study area *Quercus* sp. pollen did not exceed 20% since ~6300 cal BP (Carrión et al., 2010), while a series of similar colluvial slope deposits from other areas gave much higher contents (~40%) for the Neolithic period and only decreased below 20% after the expansion of Ericaceae during the Late Bronze Age and especially the Iron Age (Van Mourik, 1986). This discrepancy may be explained by the fact that most palynological investigations in NW Spain were performed in high-altitude peat, lake and pond deposits, where human impact was much less pronounced than in coastal areas and inland basins (Ramil-Rego et al., 1998).

In some parts of the Campo Lameiro area, wheat and millet were cultivated since the Iron Age (~2700 cal BP) (Aira Rodríguez et al., 1990; Parcero Oubiña, 2003). Nevertheless, apart from a weak signal of cereal pollen at roughly ~1500–500 cal BP, the study area did not provide evidence of intensive agricultural practices. The scarcity of ceramics and other cultural remains makes it unlikely that the area was host to significant permanent settlements as well. In Paredes, the primary activity recorded in the soils is anthropic burning to clear the land for animal husbandry. This suggests that slash-and-burn, or a less complex form of fire-involved disturbance, had a major influence on *el monte* as early as ~5500 cal BP. If this proves accurate, the profound division of the Galician rural landscape was initiated already by Neolithic societies (see also Ballesteros Arías, 2003, 2010).

The results presented in this study seem to indicate that a combination of climate change and human activities was responsible for the deforestation of the study area. The general picture is that climatic deterioration, in this study mainly following the Holocene Thermal Maximum (~5500 cal BP) and the Roman Warm Period (~1700 cal BP), mitigated the regenerative capacity of the vegetation thereby exacerbating the impact of human disturbance (fire and grazing), causing environmental degradation (reflected by erosion and deforestation). It remains extremely difficult to quantify the relative impact of climatic change and human activities. The results from the present study fit well in the accumulating body of indirect evidence of feedback mechanisms between climatic change, human impact and environmental degradation (e.g. Berglund, 2003; Fábregas Valcarce et al., 2003; Magny 2004; Magny et al., 2006; Colombaroli et al., 2008; Vannière et al., 2008; Martínez-Cortizas et al., 2009; López-Merino et al., 2010).

6. Conclusions

Pedo-anthracological analyses of colluvial soils from Campo Lameiro (NW Spain) showed that: 1) a natural forest dominated by deciduous *Quercus* covered the area from ~9500 to ~5500 cal BP, which was gradually replaced by shrub communities, 2) among the shrub species, *Erica* sp. seems to be the best indicator for fire-induced environmental degradation, 3) episodes of accelerated deforestation (~5500–5000 cal BP and ~2000–1500 cal BP) coincide with periods of increased human pressure and climate deterioration, 4) deforestation initiated on the upper part of the hill and probably had a local character, 5) in NW Spain, macroscopic charcoal records in colluvial soils seem to provide an excellent proxy for local fire-induced vegetation change.

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ANNEXES

Annex I a: Heather- and gorse-dominated shrub communities near Arzúa (A Coruña).

Annex I b: Gorse, broom and ferns in the Barbanza Peninsula (A Coruña).

Annex I c: Burnt remains of gorse that had resprouted and next level gorse resprouters, at Monte Pedroso (Santiago de Compostela, A Coruña).

Annex I d: Heather, gorse and ferns on Monte Faro (N Portugal), in 2006.

Annex I e: High-altitude (ca. 800 m a.s.l.) shrubland dominated by tree heather (*Erica arborea*) and gorse (*Ulex* spp.), from the Xistral Mountains (Lugo). Tree heather dominated the shrub communities of Galicia since ca. 2500 cal BP until being replaced largely by gorse and broom.

Annex I f: A > 1 m thick Atlantic ranker from Monte Faro (N Portugal), supporting gorse-domminated shrub communities. Charcoal fragments are abundant in this soil.

Annex I g: *O monte* landscape around Santiago de Compostela (A Coruña). Note abandoned fragmented eucalyptus plantations invaded by gorse in the background.

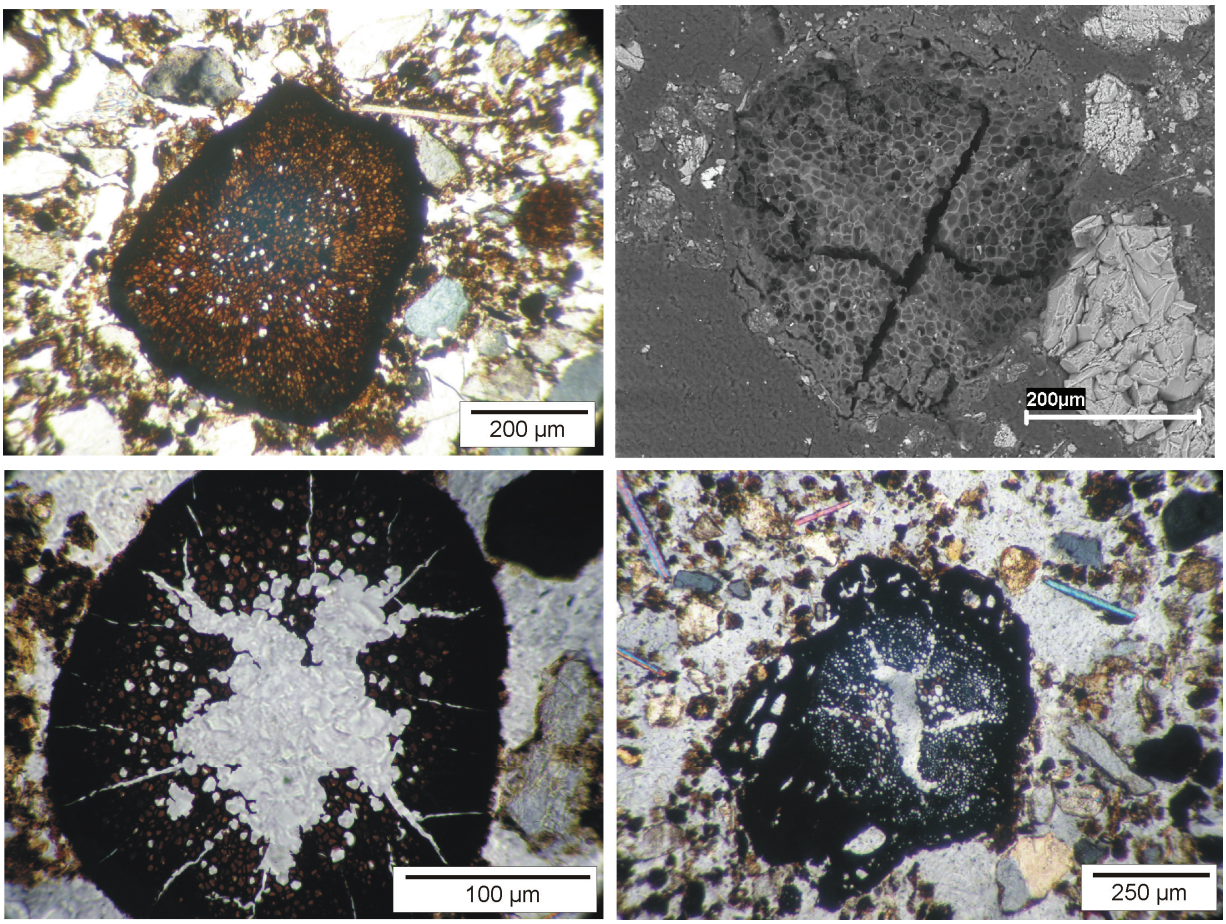
Annex I h. Flowering tree heather, heather and gorse in a typical uphill *aldea* (rural village), near Castro Caldelas (Ourense). *Photograph by P. Ballesteros Arias.*

Annex I i: Gorse shrubland, pine plantations and windmill parks near Alto dos Teares (N Portugal).

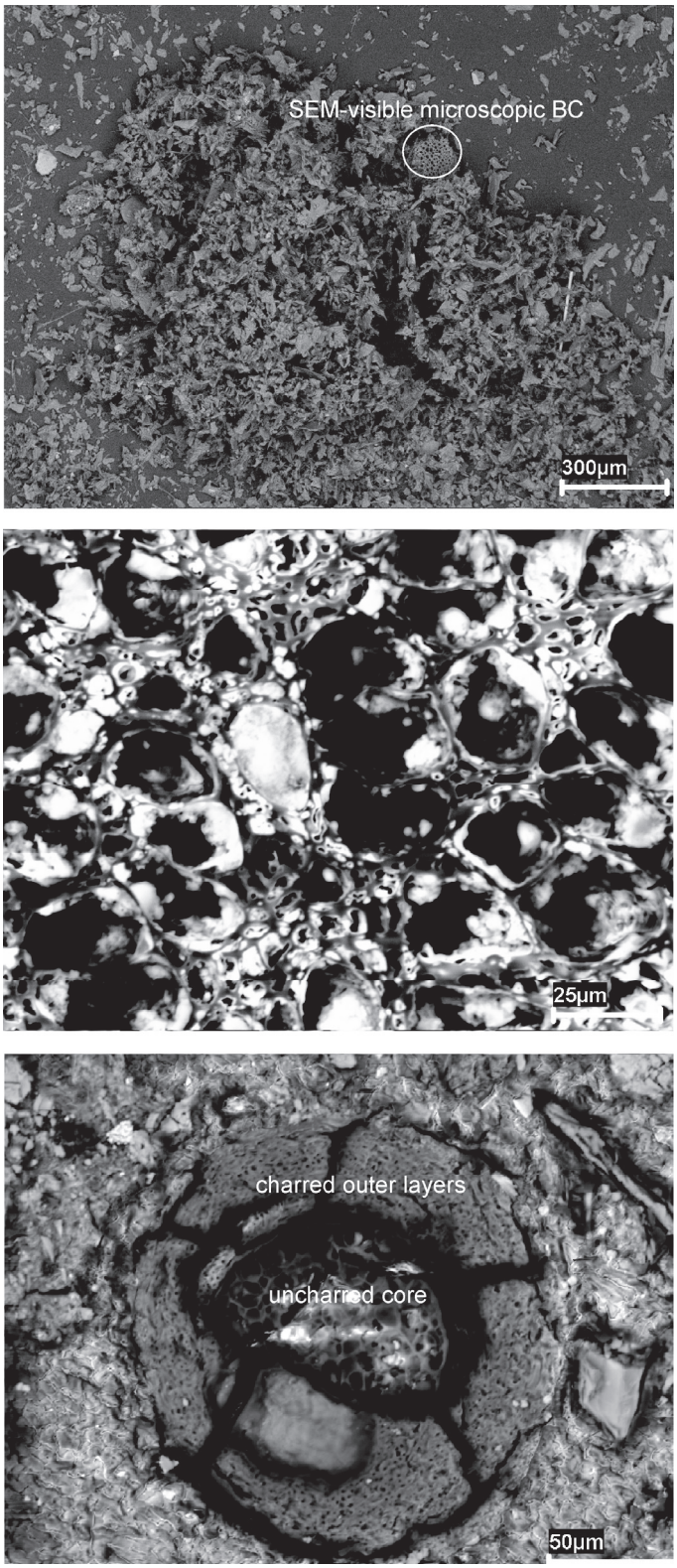
Annex I j: Broom cultivation and pasture grounds near Montouto (Lugo).

Annex I k: Shrubland fires near A Arrotea (Pontevedra) in 2006. That year, the area that was burned in Galicia amassed almost 100.000 ha, including ~25 % of the Campo Lameiro municipality, with an estimated economic loss of ca. 300,000,000 €. *Photograph by S. Grana Gestal.*

Annex II: Photographs from the Rock Art Park of Campo Lameiro (upper left:'Rock Art Capital'), showing the *Os Carballas* petroglyph (upper right), the subsurface remains of huts (lower left) from the construction site (*by F. Criado Boado*) and the construction site itself with typical shrubland species in the foreground (*Calluna vulgaris, Ulex europaeus, Pteridium aquilinum*, etc.).



Annex III: Fungal sclerotia from thin sections obtained from the colluvial soils of Campo Lameiro, probably from *Cenococcum geophilum*. Note significant degradation of the body of the sclerotia in the photograph to the lower left and possible charring and degradation of the inner core in the lower-right photograph. Upper right image is a SEM micrograph of a sclerotium embedded in the residual resin of thin section preparation.



Annex IV: SEM micrographs of BC particles. Above: NaOH-extractable SOM from soil PRD-1 with a high proportion of 'amorphous' BC. Note the SEM-visible BC microparticle (encircled). Middle: mineral coatings and concretions in aged charcoal from PRD-1. Below: partially charred material from the surface of soil PRD-2 (using a residual resin block from thin section procedure).

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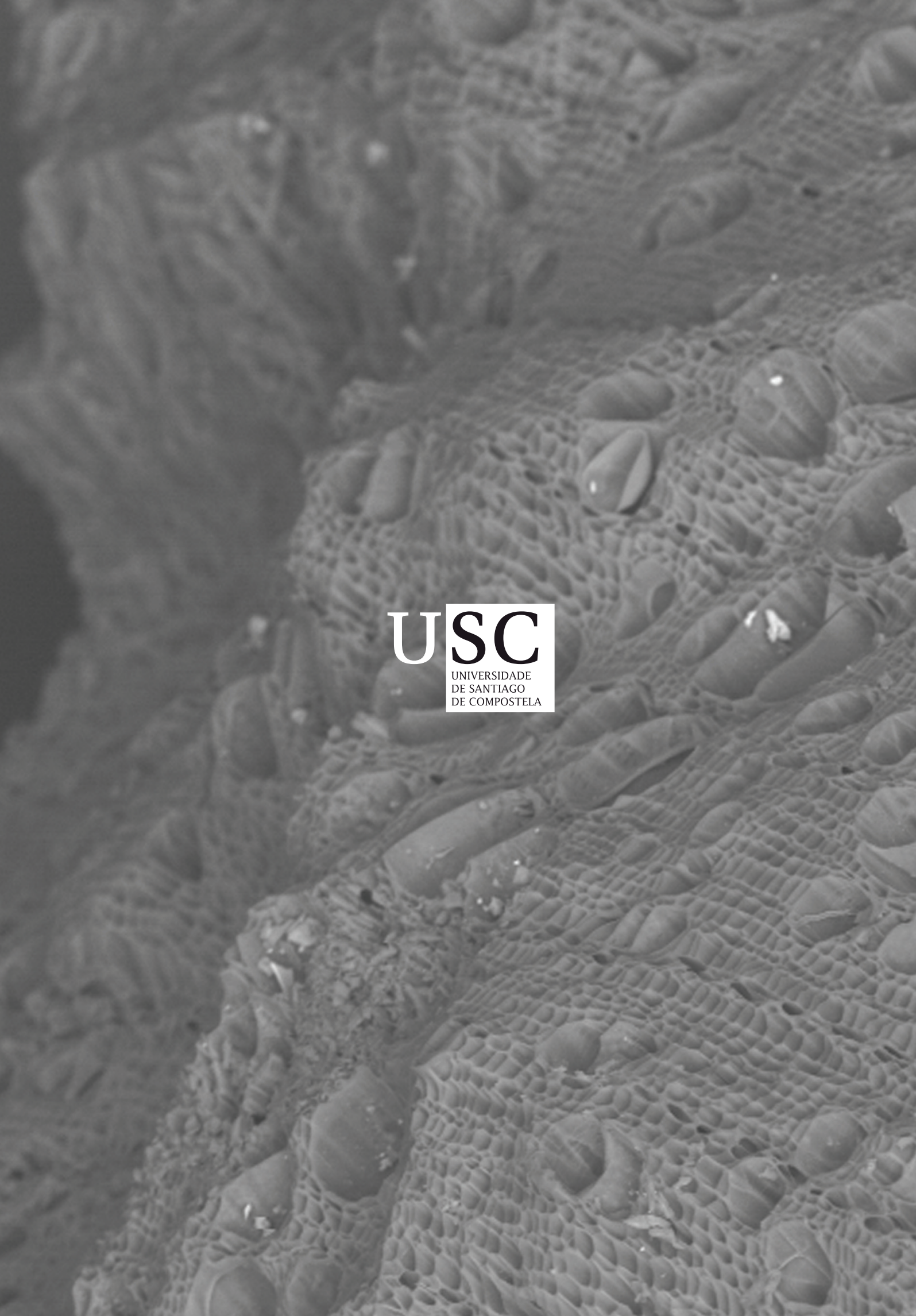
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